SYNTHESIS AND REGENERATION OF ENHANCED EGGSHELL SORBENTS FOR CLEAN COAL APPLICATIONS

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ABSTRACT

By the year 2010, global carbon dioxide emissions will reach a staggering 31 billion metric tons per year. With much of this CO_2 coming from energy production, an economical means to capture CO_2 during fossil fuel conversion is critical. One of the most promising CO_2 capture techniques employs a cyclic carbonation of CaO to $CaCO_3$ and calcination of $CaCO_3$ back to CaO. This scheme separates CO_2 into a pure stream in post-combustion and pre-combustion systems for the production of electricity, hydrogen, and liquid fuels. The challenge of this method, along with the purpose of this study is to find economical, high reactivity $CaCO_3$ sorbents.

The U.S. produces approximately 190,000 tons/yr of eggshell waste, which contains around 95% $CaCO_3$ and presents itself as an inexpensive alternative to synthetic calcium carbonate sorbents. Various acetic acid pretreatments were tested to remove the eggshell's membrane and alter the shell's pore structure. The CO_2 capture capacity for multiple strengths and durations of acetic acid pretreatments was then measured by carbonating the samples in a thermogravimetric analyzer using a 10% CO_2 stream. Finally, six strengths of acetic acid treatments were also explored to regenerate spent sorbents that had undergone a pore collapse after multiple cycles. The conducted experimentation has shown that the membrane contains highly valuable Type X collagen, as proven through proteomic analysis, which would supplement the process economics when sold. Also, it was found that a pretreatment with acetic acid facilitates the generation of a mesoporous structure, allowing the eggshell sorbent to reach higher conversions over more carbonation/calcination cycles. Finally, regeneration of spent sorbents with acetic acid solutions showed a substantial revitalization in both

recyclability and carbon capture. The combined optimization of cheaper, more sustainable sorbents for clean fossil fuel conversion, as presented here, will make the implementation of such systems a much more economical and environmentally friendly solution for future energy needs.

Dedicated to my parents, Steve and Dodie, and my fiancée, Amy, for their love and continuous encouragement to follow my dreams.

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I would also like to thank my graduate student mentor, Shwetha Ramkumar, for all of her one-on-one guidance with the process technology and help with getting acquainted with the equipment in the group. She spent a great deal of her own time helping me to become familiar and comfortable with the group. She also was a great asset in setting up my experimental design.

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CHAPTER I

INTRODUCTION

1.1 AN INTRODUCTION TO CO_2 GENERATION

In an age where environmental concerns have become increasingly prevalent, the necessity for efficient and environmentally friendly methods for supplying the world's energy has become an imperative issue. Climate instability has been a subject of major concern and, therefore, a major target of study. Increasing levels of greenhouse gases are widely regarded as a key factor in the negative shift in global climate [Wallace, 2000],[IPCC, 2007]. Greenhouse gases (GHG) serve to trap solar radiation within the atmosphere of the earth. While these gases are essential to the thermal regulation of the earth, when the concentration of these gases increases, the solar radiation that would normally be reflected into space is instead trapped within the atmosphere of the earth. This can be illustrated in Figure 1.1 below:

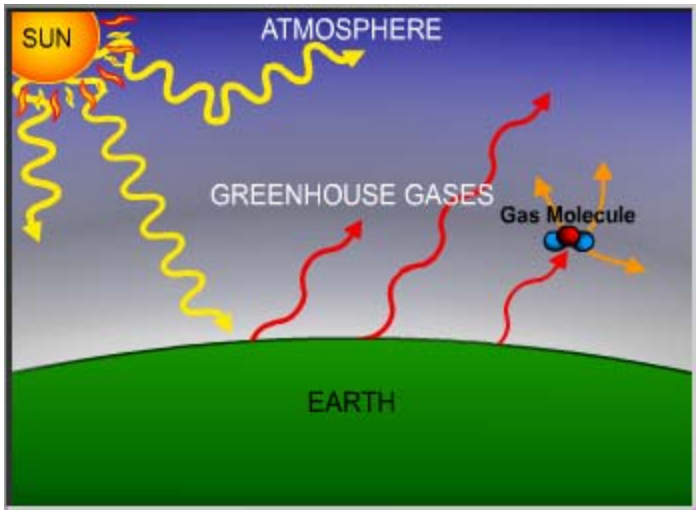

Figure 1.1: Greenhouse Gas Effects in the Atmosphere, [EPA, 1999]

The greenhouse effect, when amplified by rising greenhouse gas levels, can have broad effects on temperature and regional climate patterns [IPCC, 2007]. Without

argument, there have recently been increased levels of greenhouse gases that are unprecedented over the last 600 thousand years. This fact is best illustrated in Figure 1.2 below:

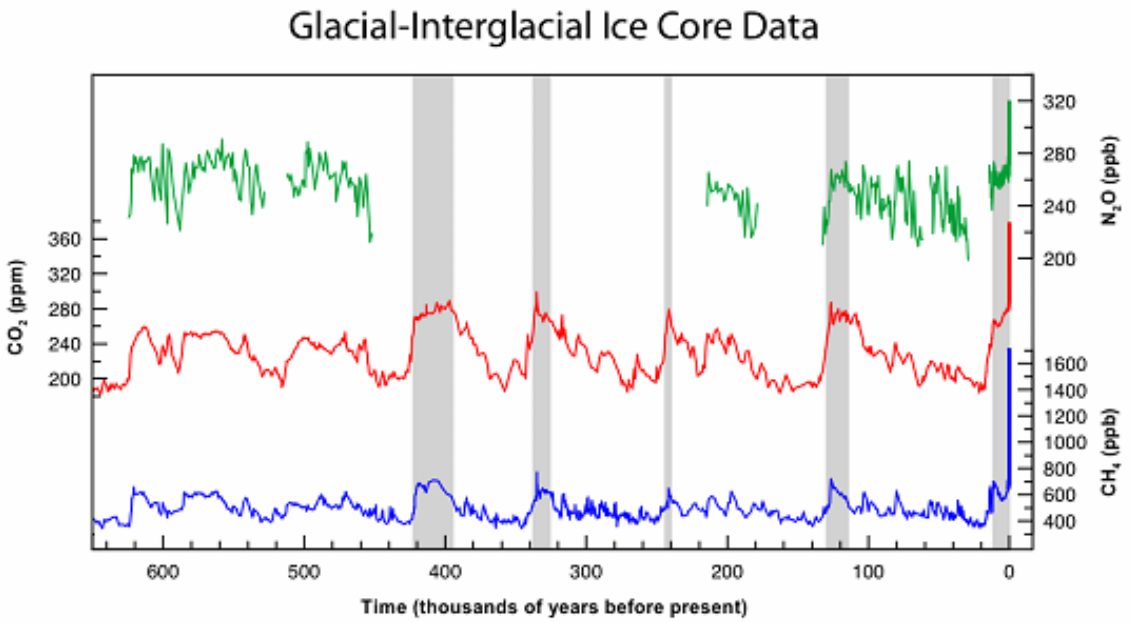

Figure 1.2: Ice Core Data Documenting Greenhouse Gas Concentrations, [Adapted from Pachuri and Jallow, 2007]

This figure clearly displays the rise in three key greenhouse gases. The notable rise in global CO_2 concentrations in the short time since the industrial revolution illustrates the necessity to control CO_2 emissions caused by human activity, known as anthropogenic emissions.

The effects on climate are already being felt around the world from the climate instability introduced by rising greenhouse gas emissions. In fact, the warmest ten years on record from before 1850 until 2006 all occurred from 1997-2006 [Pachauri and Jallow, 2007]. In order to help assess and address this problem, the United Nations formed the Intergovernmental Panel on Climate Change (IPCC). The findings from this group included many presently shifting climate conditions in addition to conditions that

were predicted to change in the coming years. Figure 1.3, below, shows shifts in global mean temperature, mean sea level, and snow cover in the Northern Hemisphere:

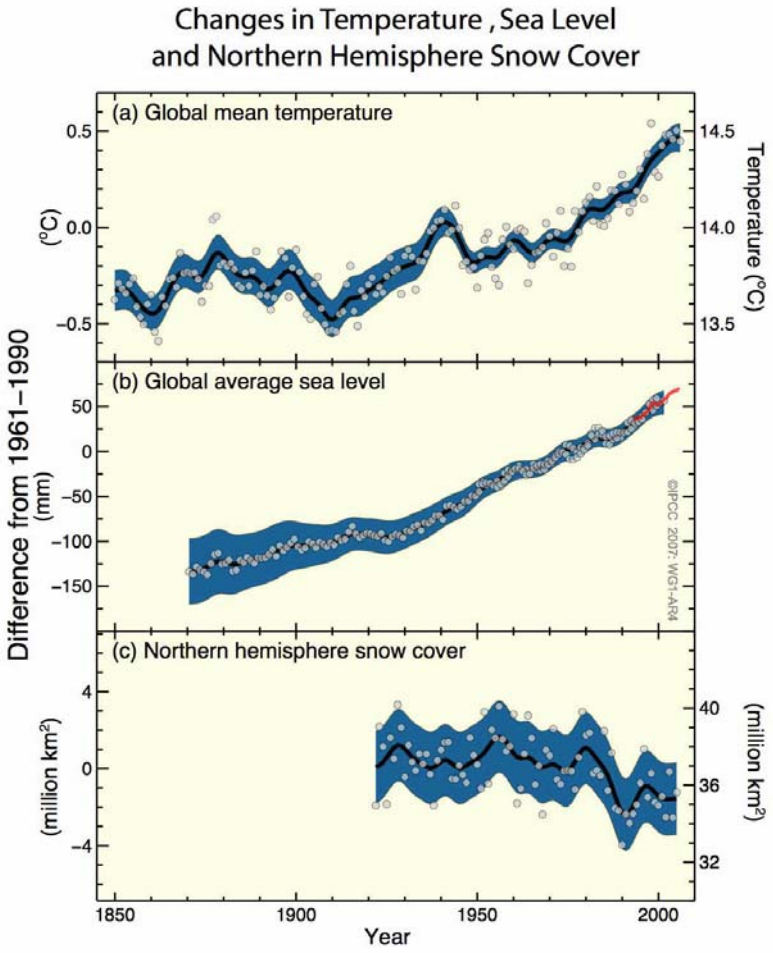

Figure 1.3: Changes in Global Temperature, Sea Level, and Northern Hemisphere Snow Cover, [Pachuri and Jallow, 2007]

In addition to continued shifts in these trends, it is also expected that the world will encounter more frequent and more extreme heat waves, increased tropical cyclones, and increased droughts in the tropics and subtropics [Pachuri and Jallow, 2007].

There are numerous sources of anthropogenic CO_2 emissions; however, most notable among these sources are emissions caused by combustion of fossil fuels for

transportation and combustion of fossil fuels for electricity generation. Fossil fuels include petroleum, natural gas, and coal. The figure below illustrates various magnitudes of GHG emissions and the major area under which they fall:

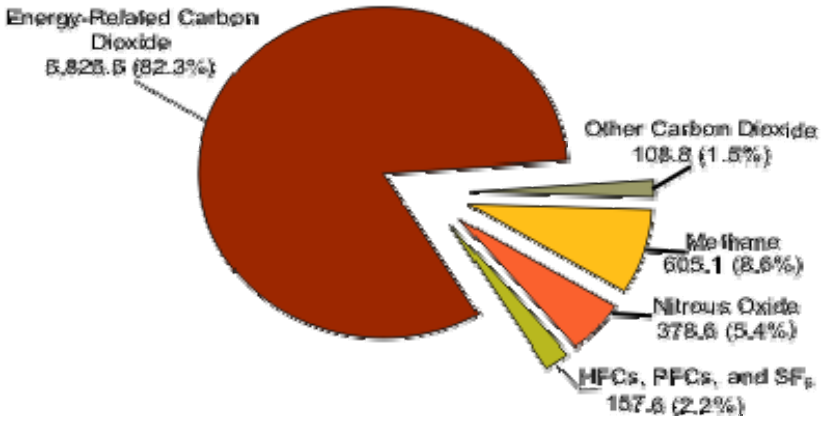

Figure 1.4: Anthropogenic Greenhouse Gas Emissions in 2006 in the United States (Million Metric Tons of Carbon Dioxide Equivalent), [EIA, 2008]

As Figure 1.4 displays, the United States' largest source of anthropogenic GHG emissions is energy-related carbon dioxide. This knowledge provides an area of focus for GHG emissions reduction. In the year 2006, worldwide carbon dioxide emissions were estimated to have ballooned to a staggering 30 billion metric tons per year, with the United States accounting for approximately 20% of this total. [EPA, 2009]. Of the 5.92 billion tons of CO_2 released in 2007 by the U.S., 5.74 billion tons were due to the combustion of fossil fuels [EPA, 2009]. Furthermore, of the 5.74 billion tons of CO_2 released from fossil fuel combustion, 2.40 billion tons of CO_2 came from the production of electricity and 1.89 billion tons came from the use of fossil fuels for transportation [EPA, 2009]. When combining these two GHG sources, they account for 74.7% of all U.S. anthropogenic CO_2 generation. Targeting these sources for technological study can help provide much needed solutions to reduce emissions of greenhouse gases within the United States.

1.2 USES OF HYDROGEN AS AN ALTERNATIVE FUEL

There are several methods that have been proposed to supplement the energy needs of the United States. While many of these include renewable energy sources, such as solar energy, biofuels, and wind power, there are numerous problems with these technologies, including, but not limited to, high costs and limited availability. Therefore, the need for a more widely available, cleaner fuel has risen as a topic of extensive research. When H_2 reacts with oxygen, the reaction is as follows:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad (1)$$

Since the only product in this reaction is water, H_2 is considered to be cleaner than fuels such as coal and other fossil fuel derived products.

Hydrogen is the most abundant element on our planet at roughly 18% atomic occurrence, however, the naturally occurring pure form of H_2 is much more difficult to find [Stiegel and Ramezan, 2006]. Coal contains about 4-6 wt% hydrogen, but by coupling clean coal techniques for gasification with this number, hydrogen production can be further supplemented. Currently, hydrogen is commonly produced from thermochemical reforming of hydrocarbons with steam and partial oxidation of fossil fuels [Stiegel and Ramezan, 2006]. Current production of hydrogen has been largely for industrial use due to its essential role in the generation of many chemicals and fuels.

In order to increase hydrogen production for the generation of electricity for 25 million homes, or, equivalently, 25 million cars, 40 million tons/yr of H_2 will be required. This is the equivalent of 140 coal gasification plants with feeds similar to that of current larger scale coal power plants [Steigel and Ramezan, 2006]. Hydrogen also has the additional advantage for electricity generation that it can be used in combination with

fuel cells. Certain types of fuel cells, known as solid oxide fuel cells, operate at very high temperatures and high efficiencies with a mild CO tolerance [Steigel and Ramezan, 2006]. These high efficiencies are achievable because fuel cells waste less useful work, instead taking advantage of electrochemical reactions to generate electricity. Due to the clean, efficient nature of hydrogen-based electricity production and the growing need for H_2 in the area of commodity chemicals production, new techniques should be explored for the generation of H_2 in the modern economy.

1.3 Calcium-Based Chemical Looping Technologies

Currently, approximately 90% of domestic electricity production takes place through the combustion of coal in pulverized coal combustion plants [Li and Fan, 2008]. This method utilizes coal combustion with air to generate heat. That heat is then used to make steam, which is then converted into electricity using a turbine. While many of the pollutants, such as sulfur, are pulled out of the emissions from these plants, there are still very large amounts of CO_2 generated by coal burning power plants, as was discussed in Section 1.1. Depending on the pressure and the quality of the steam generated, this type of plant can achieve an HHV efficiency of 33-45% for the production of electricity from coal; however, this efficiency is derated by almost a third for most plants if Monoethanolamine (MEA) is used to capture 90% of the CO_2 for sequestration due to the low temperatures of MEA process operation and high pressure needed for sequestration [Li and Fan, 2008]. This means that plants would lose 1/3 of their energy generation capacity by using MEA systems to pull CO_2 out of production flue gas streams. Until the point where there is a heavy CO_2 tax, this decision does not make economic sense for

coal-utilizing electricity companies. In addition to MEA, there are other techniques that can be used for CO_2 separation, such as Pressure Swing Adsorption (PSA) [Sarkar and Bose, 1997], and Selexol. All of these systems have costs that can increase the cost of energy by as much as 50-200% [Herzog et al., 1997].

An alternative to these systems, therefore, is to build in a mechanism that minimizes the loss of useful work required in the overall process to remove and separate CO_2. Ideally, this system should be able to do this separation at high temperature to avoid the need to warm and cool the system, minimizing parasitic energy losses to heating requirements. Because of this, there is a demand for high temperature sorbents which can be used to effectively and efficiently separate CO_2 from the products of combustion. Calcium oxide has presented itself as a strong candidate for use in chemical looping due to the temperature at which it reacts with CO_2, its good sorbent qualities, and its relative abundance [Ramkumar et al., 2008]. The calcium looping process begins with the incomplete combustion of coal with oxygen to form a mix of CO and H_2 known as synthesis gas (or syngas). A diagram detailing these flows can be found in Figure 1.5. The syngas is mixed with steam and enters the water gas shift reactor, where the water gas shift reaction occurs in addition to reactions with numerous other pollutants.

Water Gas Shift Reaction: $CO + H_2O \rightarrow H_2 + CO_2$

Carbonation Reaction: $CaO + CO_2 \rightarrow CaCO_3$

$$CaO + H_2S \rightarrow CaS + H_2O$$

$$CaO + COS \rightarrow CaS + CO_2$$

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

This allows for an integrated method for removing numerous pollutants simultaneously in a single reactor. Also, since the equilibrium of the water gas shift reaction is not fully toward completion, pulling CO_2 out of the reactor pushes the reaction towards completion by Le Chatelier's Principle. This means a pure H_2 stream can be produced as a product of the process with the yield enhanced by CO_2 removal. This process is illustrated by Figure 1.5 below:

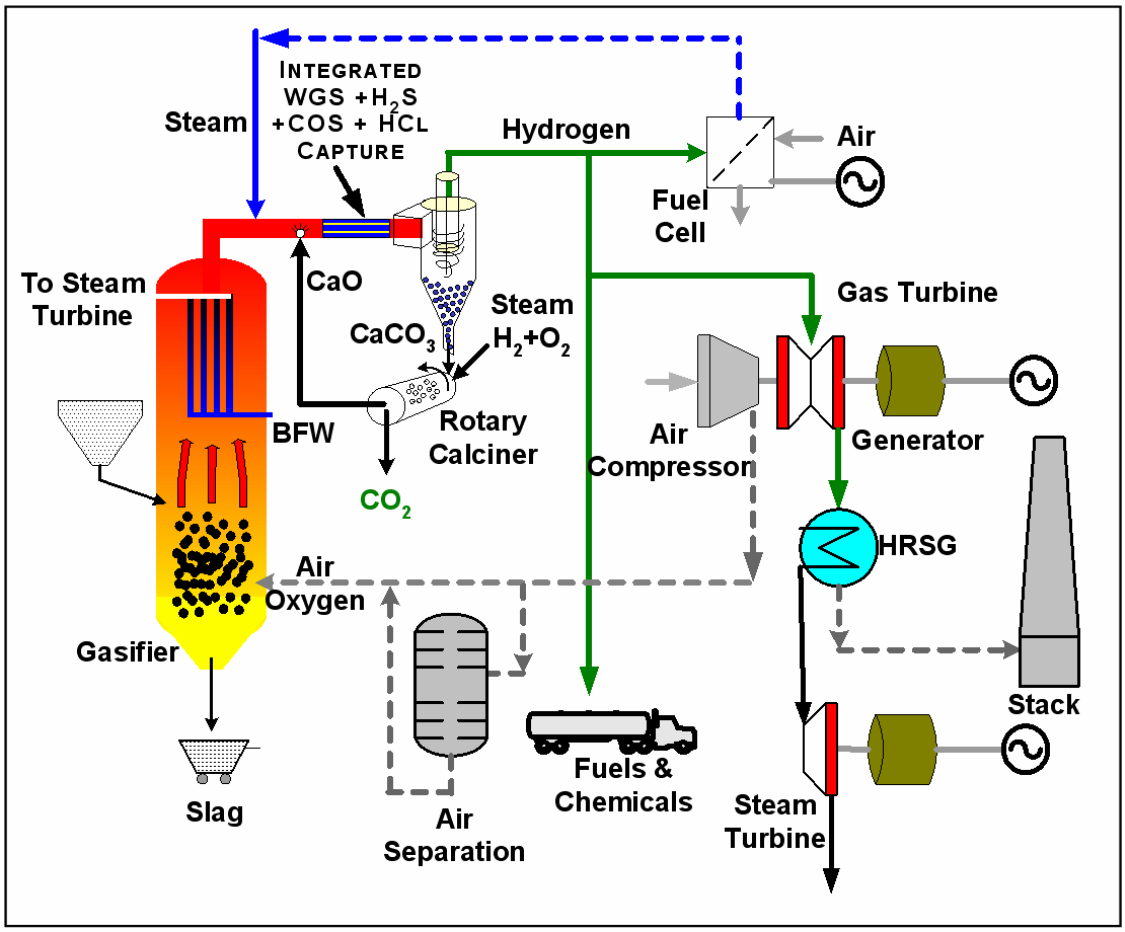

Figure 1.5: A Depiction of the Overall Flow for the Calcium Looping Process in a Coal Gasification Plant [Ramkumar et al., 2008]

The solid $CaCO_3$ can then easily be removed from the H_2 product gases. The CaO particles for the process can then be regenerated through the calcination reaction:

$$Calcination: \quad CaCO_3 \rightarrow CaO + CO_2$$

Modeling of the system shows that this set-up, with proper heat integration, can have an HHV efficiency of 63% [Fan et al., 2008]. This means that the process can offer competitive solutions for generation of electricity by sending the hydrogen generated to either a combined cycle power generation system to harvest the energy and heat from hydrogen combustion or to a solid oxide fuel cell where the energy is converted electrochemically into electricity.

1.4 Project Targets

In order to find effective sorbents for the calcium looping process, several targets must be considered for optimization:

- Find an inexpensive, high reactivity CaO sorbent source for use in calcium looping
- Synthesize an optimal pretreatment that gives the sorbent the highest initial reactivity.
- Optimize the sorbent's recyclability since the particle will need to undergo many cycles in the process to lower operation costs of the plant
- Investigate regenerations to revitalize sorbent performance
- Identify additional economic drivers for use of the specified sorbent

By investigating these parameters, an important problem can be answered in the quest to reduce carbon emissions through clean fossil fuel conversion technologies.

CHAPTER 2

TECHNOLOGICAL REVIEW

2.1 CALCIUM OXIDE SORBENTS

Utilizing $CaCO_3$ provides an ideal solution to process integration in clean coal processes because it allows for carbonation and calcination at higher temperatures than most other metal carbonate candidates [Gupta and Fan, 2002]. Optimization of calcium oxide sorbents is a key step to address in effectively assessing the viability of chemical looping processes for clean coal technology. Perhaps most important to the success of this technology is the generation of an inexpensive sorbent that can undergo numerous carbonation/calcination reactions (CCR's). Because the molecular volume of $CaCO_3$ is much larger than CaO, 36.9 and 16.9 cm^3/mol respectively [Yrjas et al., 1996], the surface of CaO sorbents can be subject to pore plugging, known as sintering, after several cycles, preventing CO_2 from diffusing through and reacting with all CaO present. Sintering is a process that occurs in CaO sorbents at elevated temperatures whereby a surface reorganization causes the particles to agglomerate, reducing surface area and effective CO_2 capture. This can be remedied through the generation of a more porous surface structure with larger pore volumes [Wu et al., 2002]. One method by which the initial particle pore structure can be expanded is through treating it with acetic acid. Acetic acid treatments expand the pore structure by the acid reacting with $CaCO_3$ to form $Ca(C_2H_3O_2)_2$ (calcium acetate) [Sasaoka et al., 1997]. Since calcium acetate has a larger molecular volume than $CaCO_3$ and CaO, the pore structure is better retained even after multiple CCR cycles. Sasaoka et al (1997) also observed that decreasing acetic acid

concentrations increased capture of SO_2 in CaO sorbents due to the reaction mechanism between acetic acid and $CaCO_3$, which is enhanced by the presence of H_2O.

It has been documented that CaO derived from calcium acetate displays the highest conversion in the carbonation reaction of CaO among the CaO precursors tested in literature [Lu et al., 2006]. This is illustrated in the figure below:

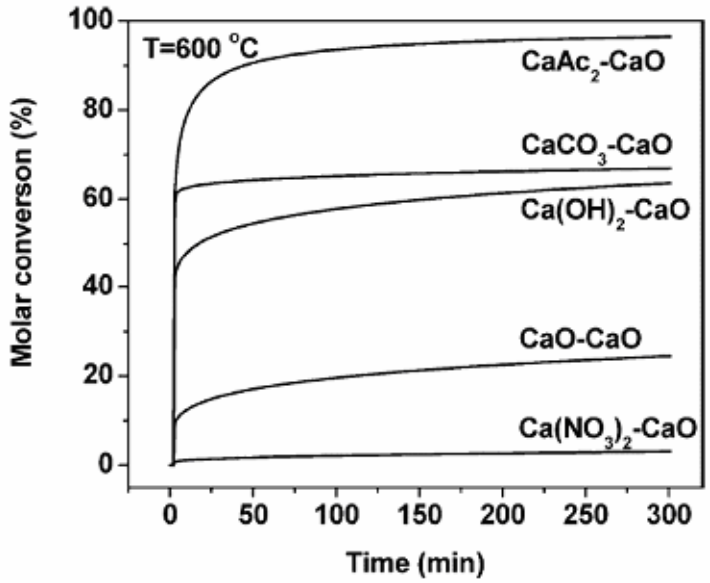

Figure 2.1: Carbonation Conversion of CaO Derived from Several Sources [Lu et al., 2006]

This figure clearly displays that CaO precursor plays a large role in the carbonation reaction of CaO. Because calcium acetate derived CaO displayed the highest conversion, treatments and regenerations employing the use of acetic acid were considered as very favorable when setting up the experimental design.

2.2 Viability of Eggshells as a Calcium Carbonate Source

While there are many different viable sources of calcium carbonate, one in particular will be investigated in the course of this study. While synthetic sorbents have been shown to be strong candidates for calcium looping, their cost is somewhat

prohibitive. However, there is an attractive, low cost alternative: the simple chicken eggshell. Each year, the United States produces roughly 190,000 tons of eggshell waste [Miller, 2001]. Shells from commercial hatcheries and egg processing facilities could easily be treated for use in the calcium looping process as a supplemental calcium source. Instead of paying $50 or more a ton to dispose of the shell, it could be sold as a product instead. Eggshells from industrial hatcheries and food processing facilities are approximately 95% $CaCO_3$ by weight [Yamamoto et al., 1997] and are commonly disposed of in industrial landfills at a cost to the company. Additionally, the surface is a natural bioceramic, meaning that it is both non-toxic and bio-inert or bio-active. Bio-inert compounds are those that do not interact with the surrounding biological systems. Bio-active compounds, like calcium carbonate, can interact, but remain robust amongst biological systems. The natural surface of the eggshell is very durable. This is because it is a calcium-based metal carbonate with a naturally binding organic matrix that helps to hold it together and give it support [Butcher et al., 1996]. Overall, this structure allows the eggshell to act as an ideal agglomerated sorbent. Due to its mechanical toughness, it can withstand numerous cycles and can more easily be separated from fly ash in the cyclone separator (shown in Figure 1.5) due to its larger particle size when compared to traditional ground limestone.

In order for eggshells from egg processing facilities around the country to be used for this purpose though, the eggshell membrane must be removed. The membrane that surrounds the inner surface of an egg contains many proteins such as collagen types I, V, and X, osteopontin and sialoprotein [Yi et al., 2004]. Collagen is of particular interest especially given that, depending on purity, it can be sold for up to $1000 per gram and

comprises approximately 10% of the eggshell membrane's mass [Yi et al., 2004]. Given that there is approximately 0.25 g of protein per membrane, extracting collagen from waste eggshell membranes could prove to be a very beneficial and lucrative process. Separating the two components of discarded waste eggshells, for these reasons, offers a thrifty alternative to merely creating additional landfill waste or utilizing the shell for animal feed filler.

The proteins within the eggshell itself have several uses. While collagen can be utilized for a range of applications, from cosmetic treatments to skin grafts for burn victims, the proteins can also be solubilized using 3-mercaptopropionic acid and 10% acetic acid at 90 ºC [Yi et al., 2004]. The solubilized eggshell proteins can actually act as an ideal cell growth substrate, performing even better than the typically employed pure collagen [Yi et al., 2004]. If purification of individual membrane components is more economically favorable than sale of solubilized eggshell proteins then there are several options for scale-up of protein purification. Differential salt precipitation has been proven to precipitate various collagen types at different salt molarities using sodium chloride or other salts [Rucklidge et al., 1996]. Also, column chromatography offers a good solution to scale-up in which a wider variety of pure proteins can be separated and sold. It is recognized as being one of the few solutions for high resolution, high throughput protein separation [Bonnerjea and Terras, 1994]. Overall, using the common chicken eggshell offers a viable solution to turning a waste into a value added product.

CHAPTER III

EXPERIMENTAL PROCEDURE

3.1 EGGSHELL SAMPLE PRETREATMENT

In order to prepare eggshell samples for characterization, several strengths of acetic acid solutions were mixed from glacial acetic acid, sourced from Fisher Scientific (99.9% pure, Lot No. 055793), and deionized water, sourced from the OSU Chemistry Stores. This mixing took place in a Pyrex 1.000 L bomb flask to enhance accuracy of mixed solutions. The eggs were sourced from a local supermarket. In order to test both ease of removal and the effect of pretreatment on eggshell carbonation conversion, acetic acid strengths were chosen which would allow the membrane to be effectively removed and would employ pretreatments identified from previous work [Sparks, 2005; Vonder Haar, 2007] as likely prime candidates for optimal carbonation. While most of these candidates were not directly studied in previous experimentation, it was found that, in general, lower strengths and lower exposure times were ideal for the generation of an optimal surface structure [Sparks, 2005; Vonder Haar, 2007].

The experimental procedure for the eggshell sample pretreatment was designed to closely mimic what would be achievable through an automated system in a production facility. In previous lab-scale methods, much more manual interaction was required due to a lack of a proper acetic acid separation method after the trial was complete and because the eggshells were dried before testing [Sparks, 2005; Vonder Haar, 2007]. This technique was observed to delay the detachment of the membrane from the shell and also decrease the degree of membrane detachment. The pretreatments will be referred to in

terms of the strength of acetic acid the exposure time for the purposes of this study. The technique for eggshell pretreatment is outlined in the following paragraph:

The samples were prepared by taking the shell of one egg (~5.5 g) and adding it to a beaker containing 200 mL of acetic acid solution. The shell was then mixed in the beaker with a stir bar for the period of time laid out in the experimental design (which will be discussed in Section 3.3). When the stir bar would get stuck or if the eggshell was trapped on the surface where it could not be mechanically agitated, the system would be manually mixed. After the desired reaction time, the sample would immediately be filtered and rinsed with deionized water to halt the reaction of acetic acid with the shell. The separated shell and membrane were then combined in another beaker. This beaker was filled with deionized water. The buoyancy difference between the denser shell and neutrally buoyant membrane allowed for the membrane to be removed from solution and dried separately from the eggshells. A figure of the eggshell mixing and buoyancy difference between shell and membrane is shown in the following figure:

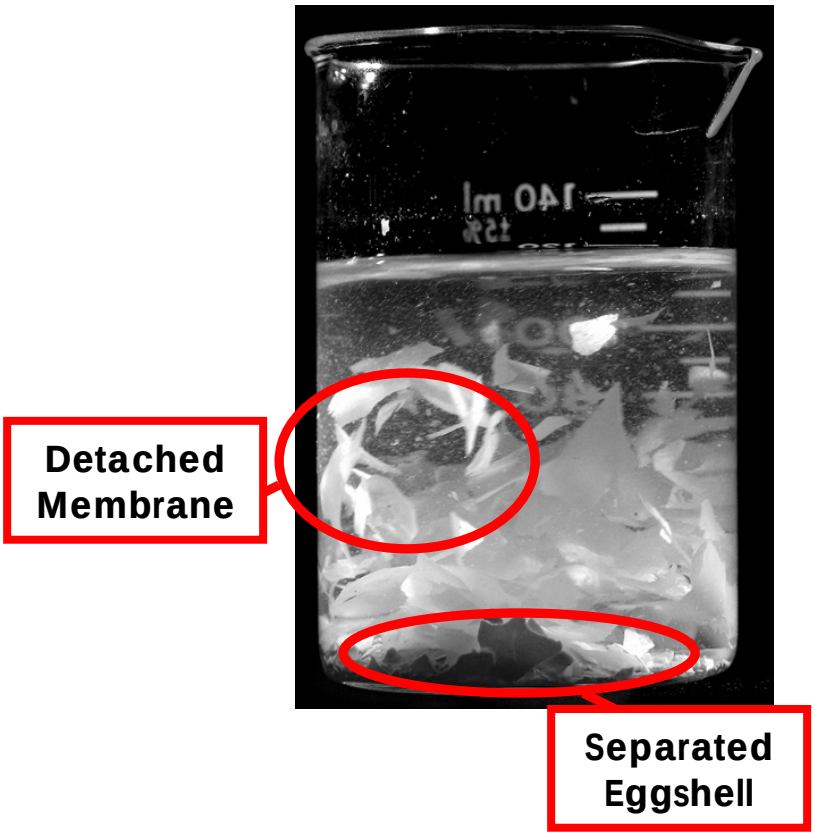

Figure 3.1: Beaker Containing Separated Shell and Membrane [Modified from Vonder Haar, 2007]

3.2 Regeneration of Spent Eggshell

It was determined that spent sorbent which had undergone a pore collapse would require regeneration in order to be feasible in industrial settings. For this reason, it was determined that some form of regeneration would be required in order to increase the conversion of the CaO in carbonation reactions. As was discussed earlier in the Technological Review, $Ca(OH)_2$ and $Ca(C_2H_3O_2)_2$ were both identified as good molecules through which to execute a pore expansion. Since both of these molecules have a larger molecular volume than CaO, the decomposition back to CaO will yield a more porous structure than was present before regeneration. To explore a variety of regeneration treatments, appropriate acetic acid solutions were again mixed and stored.

The acetic acid regeneration treatments tested involved deionized water, 0.50 M, 2.0 M, 5.0 M, 50%, and glacial acetic acid. In order to regenerate the sample, the solution was added dropwise to the calcined eggshell until the entire surface of the shell was covered. The samples were not soaked in the solution due to calcium acetate's solubility in water, which can cause the samples to dissolve. The samples were then dried either using a desiccant or by placing them in a 125 ºC furnace to fully evaporate off any excess water or acetic acid.

3.3 Experimental Design

In order to maximize the data that could be effectively gained from conducting experimentation, care was taken to develop the experimental design that would generate the most useful data. It was necessary to not only explore which pretreatment gave the optimal initial five cycle carbon capture, but also which regeneration provided the best solution to multicyclic regenerations after the sorbent reactivity declined. Since conversion decreased by approximately 40% after five cycles, it was determined that, in an industrial setting, a regeneration would be needed at this point to prevent further parasitic energy losses due to low conversion.

In order to gain some level of understanding into the effect of regeneration at different levels of pretreatments, each regeneration was conducted on both 1M, 15 minute pretreated eggshells and 1M, 30 minute pretreated eggshells. Also, a trial was conducted to perform a replicate at an identical regeneration and pretreatment in order to establish the repeatability of results. A trial was also completed to regenerate sorbent that was carbonated instead of calcined. This meant that the acetic acid would not be able to react

as fully to form $Ca(C_2H_3O_2)_2$ throughout the structure and could have different effects on recyclability and reactivity data for the sorbent. Each trial undergoing regeneration was regenerated three times so that a total of four separate five cycle runs would be completed on each type of shell. After this was completed, an optimal regeneration was determined. The remaining three pretreatments were then only run with the optimal treatment.

To gain further data about the effect of longer periods between regeneration, three samples that had undergone 20 cycles were then regenerated a fourth time and subjected to 30 cycles of additional testing to discover the long term implications of regeneration on sorbent structure. Finally, as a means of comparison raw shell which had the membrane removed manually was subjected to 10 CCR cycles.

A summary of all testing is shown in the table below:

Table 3.1: Experimental Design of Eggshell Testing

Sample ID	Pretreatment	3 Regenerations (Cycles 6-20)	30 Cycle Run (Cycles 21-50)
1	1M, 15 Minute	H2O	-
2	1M, 15 Minute	0.5 M	-
3	1M, 15 Minute	2M	-
4	1M, 15 Minute	2M Replicate	-
5	1M, 15 Minute	5M	-
6	1M, 15 Minute	5M Carbonate Regeneration	-
7	1M, 15 Minute	50%	-
8	1M, 15 Minute	Glacial Acetic Acid	-
9	1M, 30 Minute	H2O	-
10	1M, 30 Minute	0.5 M	-
11	1M, 30 Minute	2M	-
12	1M, 30 Minute	5M	5M
13	1M, 30 Minute	50%	-
14	1M, 30 Minute	Glacial Acetic Acid	Glacial Acetic Acid
15	1M, 60 Minute	Optimal Regeneration	-
16	1M, 60 Minute	No Regeneration (Just First 5 Cycles tested as Replicate)	-
17	2M, 15 Minute	Optimal Regeneration	-
18	2M, 15 Minute	No Regeneration (Just First 5 Cycles tested as Replicate)	-
19	2M, 30 Minute	Optimal Regeneration	Optimal Regeneration
20	2M, 30 Minute	No Regeneration (Just First 5 Cycles tested as Replicate)	-

3.4 Sample Characterization

3.4.1 Thermogravimetric Analyzer Set-up

In order to measure the multicyclic reactivity of the eggshells, a Perkin Elmer, Pyris 1 Thermogravimetric Analyzer (TGA) was used to measure mass change of the solid phase at various temperatures with varied gas flows. The thermogravimetric analyzer was run such that it would allow 30 minutes for the sample to carbonate and 30 minutes for the sample to calcine for each run. The gases for testing were 99.998% pure and sourced from The Ohio State University Gas Stores. A total of 120 mL/min (STP) was kept flowing through the reactor at all times. When the sample was calcining, this

was achieved through a 60 mL/min flow of N_2 to the dome of the TGA, a 48 mL/min sample N_2 flow, and a 12 mL/min N_2 balance flow. When the sample was carbonating, the 12 mL/min N_2 balance was switched to a 12 mL/min flow of CO_2. The flow line-up was controlled by a Valco Instrument Company, Inc. multiposition actuator. A diagram of the flow line-up is shown in the figure below:

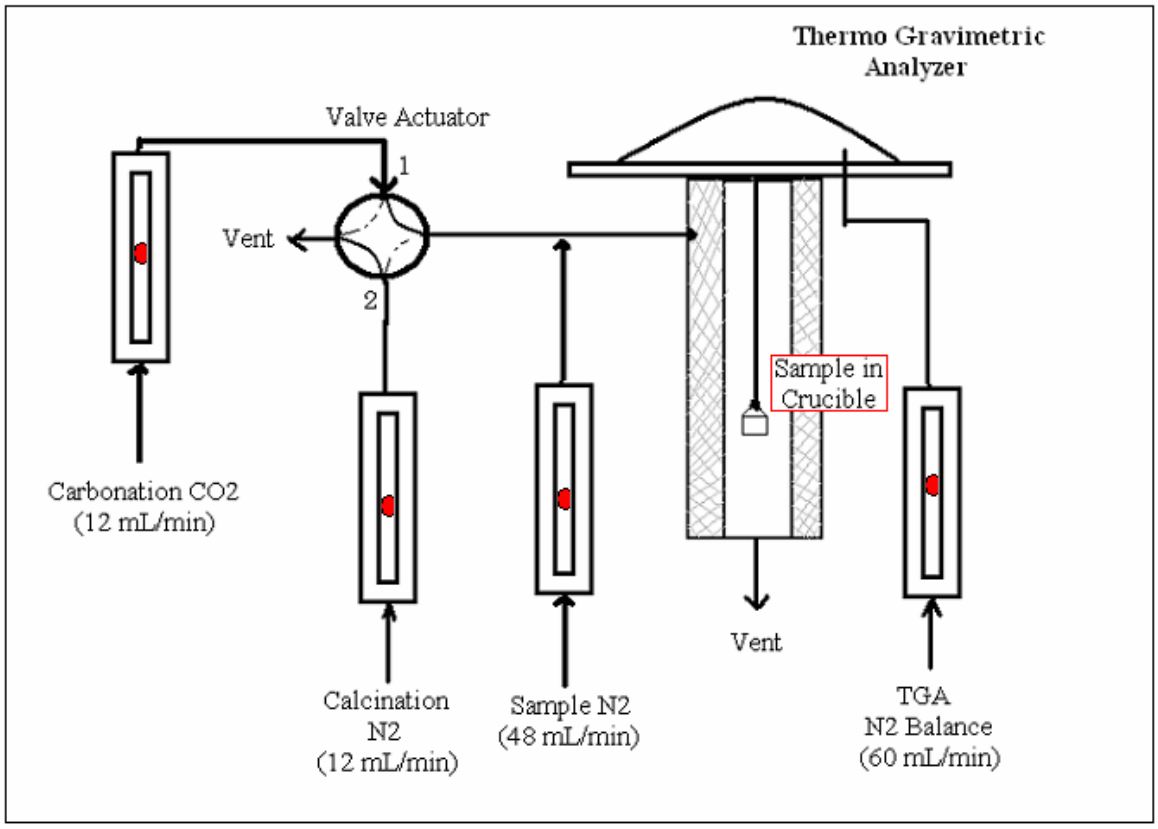

Figure 3.2: Multi-cyclic Thermo Gravimetric Analyzer Set-Up [Modified from Vonder Haar, 2007]

For the purpose of experimentation, all carbonation and calcination reactions were kept at 700 ºC for the TGA. In order to assess the conversion of the CaO to $CaCO_3$, the following equation is used:

$$Conversion = \frac{(Current\_Mass - Calcined\_Mass) * MW_{CaO}}{Calcined\_Mass * MW_{CO_2}} * 100\%$$

3.4.2 FIXED BED SET-UP

In order to test the use of eggshells as an alternative sorbent for enhancing the yield and purity of H_2 from methane, a fixed bed set-up was employed. The fixed bed, like the thermogravimetric analyzer, was run at atmospheric pressure. Approximately 3.00 g of eggshell, measured using a Denver Instruments M-220 Balance, was lightly ground into smaller chunks to fit into the reactor. This was mixed with 3.00 g of ground Performax methane reforming catalyst from Süd-Chemie Inc. (Louisville, KY) and packed into the fixed bed between layers of quartz wool. The sample was then calcined in the reactor at approximately 700 ºC for 4.5 hours with a mild flow of N_2 to carry away CO_2 formed. The temperature of the reactor was lowered to 650 ºC and the catalyst was then activated for approximately 2 hours using hydrogen. The methane steam reforming reaction was carried out at 650 ºC by sending a 5:1 ratio of steam to methane into the reactor. The products were then measured through the use of gas analyzers to measure CO_2, CO, and methane flows. A flow set-up for the system can be seen in Figure 3.3:

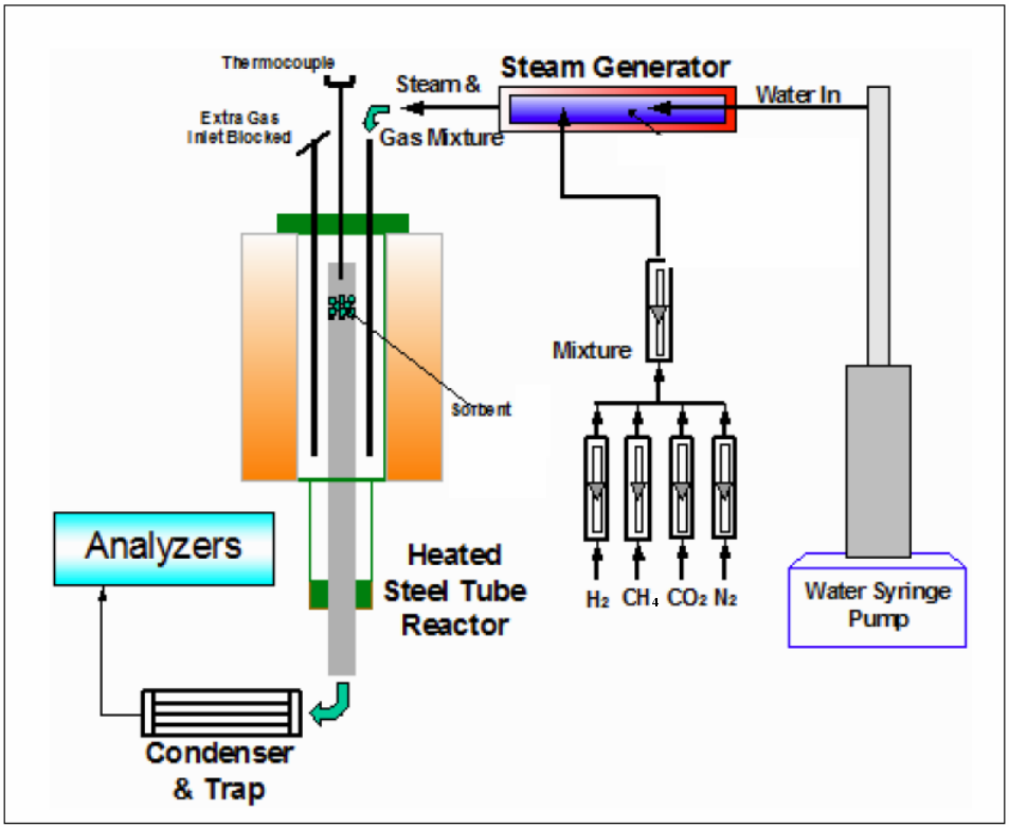

Figure 3.3: Fixed Bed Reactor for Methane Steam Reforming [Modified from Vonder Haar, 2007]

3.4.3 PROTEOMIC TESTING

In order to measure the amount and type of collagen present in the eggshell membrane samples, several techniques were employed at The Ohio State University Mass Spectrometry and Proteomics Facility. The acetic acid solution used from shell pretreatment was tested before and after being concentrated using a spin filter. Concentrating the solution allowed for better testing of more dilute proteins dissolved in the acetic acid. Several methods were employed to dissolve membrane proteins of pure eggshell membrane that was also delivered to the facility in order test for protein presence using gel electrophoresis. The "bands" on these gels that appeared to line up

with appropriate molecular weights for collagen were then tested in a SwissProt Unlimited protein analyzer for identification.

3.5 SAFETY

Precautions were taken at every step to ensure safe lab practices were upheld in all possible instances. All high pressure gas cylinders were routinely checked for leaks using a soapy water solution. Additionally, when dealing with hot reactors and furnaces, proper insulating gloves were worn at all times that the item to be handled was above 50 ºC. Other standards for the use of personal protective equipment (PPE) were also employed. Since acetic acid vapors can be quite dangerous, anytime high strength acetic acid solutions were used, the acid was mixed and kept in a fume hood. Also, nitrile gloves and safety glasses were worn when handling all acids. Finally, since the Performax catalyst used for reforming has been identified as a possible carcinogen, proper gloves and masks were worn at all times that the catalyst was handled.

CHAPTER IV

RESULTS AND DISCUSSION

Experimentation was conducted on eggshells in order to assess the feasibility of their use in calcium looping processes for clean fossil fuel conversion applications. This testing involved both an optimization of the initial eggshell pretreatment and an optimization of the eggshell's regeneration using varying acetic acid concentrations. The mechanics of the membrane removal system will be discussed in detail in the first section of this chapter. Then, in order to assess the feasibility of in-process systems for hydration and acetic acid treatment, thermodynamic analysis was executed and is covered in the second section. The results obtained from the study of the effect of pretreatment on capture capacity will be addressed in the third section. The fourth section addresses the feasibility of eggshell regeneration and effect on carbon capture. The fifth section details of the use of eggshell as a calcium sorbent in methane steam reforming to enhance conversion. Finally, the sixth section examines the findings related to the separation and purification of collagen from eggshell membranes.

4.1 MECHANICS OF MEMBRANE REMOVAL

In order for the process of initial shell processing to be effective, the membrane must be effectively and completely removed and separated. Though this was initially performed through carrying out the pretreatment on the dried shells and manually separating the shell and membrane, this system was difficult to automate due to the level of manual interaction required with the system. In an effort to make the system more easily automated, the eggshells were treated when the membrane was still moist. By

doing this, it was found that avoiding the drying of the shell greatly increased the ease of membrane removal. For this reason, when processing eggshells in industrial facilities and hatcheries, the eggshell should be kept hydrated in a holding tank filled with water until shell processing can be completed in the batch removal system.

In order to separate the shell from the membrane, the shells were initially placed in a beaker of distilled water after weighing. They were then mixed for the prescribed amount of time. It was observed that, during normal mixing, the still hydrated membranes could be thoroughly removed in less than 15 minutes with a 1 M acetic acid treatment. It was also observed that the release of the membrane from the shell occurred when the shell encountered turbulence in the liquid or bumped into other solid particles. This helps to establish the necessity of turbulent mixing in the scale-up of the membrane removal. Once the treatment was complete, the solution was poured through a course filter. The shell and membrane were then combined and mixed for a short period of time in pure deionized water. This allowed the shells to settle to the bottom while the membrane was dispersed throughout the liquid. From here, a sieve could be used to separate the membrane pieces from the solution. The separated shell could then be removed from the bottom. If this separation is attempted while the shell is still in the acetic acid solution, the CO_2 from the reaction of $CaCO_3$ with acetic acid causes the shell to rise to the surface, making separation difficult. A heavier liquid can be used to make the membranes more buoyant, however, an addition of salt may cause dissolved membrane proteins to precipitate [Rucklidge et al., 1996], lowering the purity of the separated shell. In order to carry out the procedure on an industrial level, relatively little equipment is needed. A diagram detailing a rough set-up is shown below:

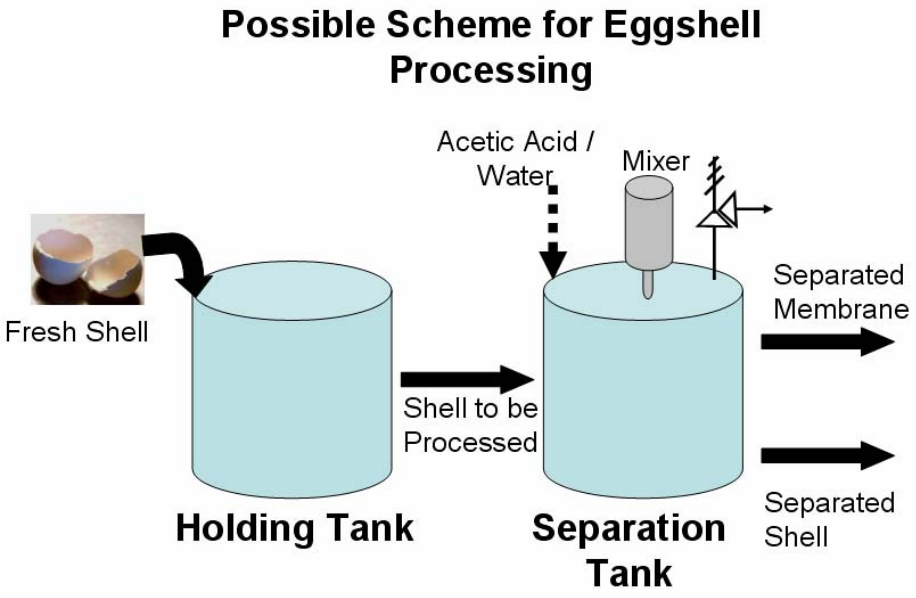

Figure 4.1: Proposed System for Industrial Set-Up

This scheme would allow for optimal mixing and separation. The following is a possible procedure for running the scheme:

1. Deposit fresh eggshell into the holding tank to wait for further processing.
2. Transfer batch of fresh shell to separation tank containing acetic acid solution.
3. Mix for desired amount of time determined by process economics and membrane separation.
4. Drain acetic acid solution out of the tank, allowing membrane and shell to remain within the tank. The acetic acid solution can be readjusted to the desired molarity and be maintained for further treatments rather than being discarded.
5. Fill the separation tank with water.
6. Stir lightly for a short period of time to enhance suspension of membrane.
7. Use a mesh to filter the membrane out of the suspension.

8. Drain water and collect shell from the bottom of the separation tank for drying and sale.

This scheme, based on observed practices of separation on the lab-scale level, should provide adequate shell separation with the smallest possible cost in capital and space. This would allow the system to be readily added to existing egg processing facilities with minimal cost.

4.2 Thermodynamic Considerations

When assessing the feasibility of implementing shell regeneration systems on the commercial scale in clean coal facilities, it is necessary to observe whether or not the system for hydration and calcium acetate formation can occur at elevated temperatures. The thermodynamic analysis will be used to show three key objectives of the process set-up: (1) the hydration reaction of CaO will not take place during carbonation, (2) the hydration reaction is achievable at elevated temperatures, and (3) the formation of calcium acetate is possible at elevated temperatures. In order to maximize the reactive effects of sorbent regeneration, CaO should be regenerated from the fully calcined sorbent, not the carbonated sorbent from the Water Gas Shift Reactor.

It is important to establish that hydration will not compete with carbonation in the Water Gas Shift Reactor in order to ensure that this side reaction won't lower the amount of sorbent available for carbonation. In order to prove this, the equilibrium data for the hydration of CaO was utilized at atmospheric pressure with an equilibrium partial pressure of H_2O plotted versus temperature. Figure 4.2 shows that the hydration reaction is not favorable above approximately 500 ºC, even with nearly pure steam.

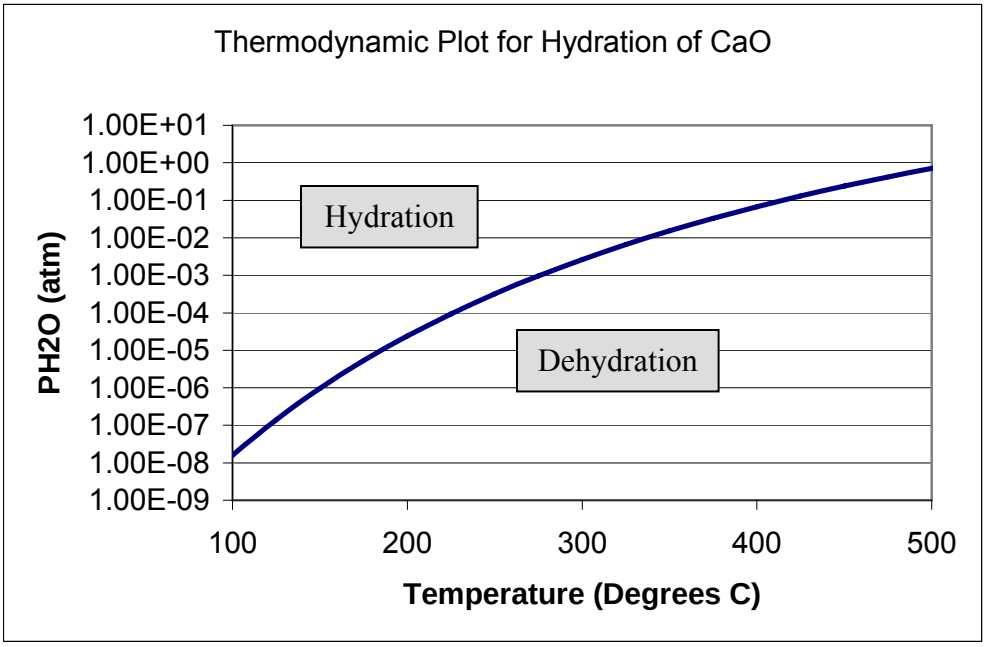

Figure 4.2: Thermodynamic Plot for Hydration of CaO [1 atm total pressure]

It is also necessary to analyze the plot for the carbonation of CaO to examine appropriate carbonation temperatures. This is shown below in Figure 4.3:

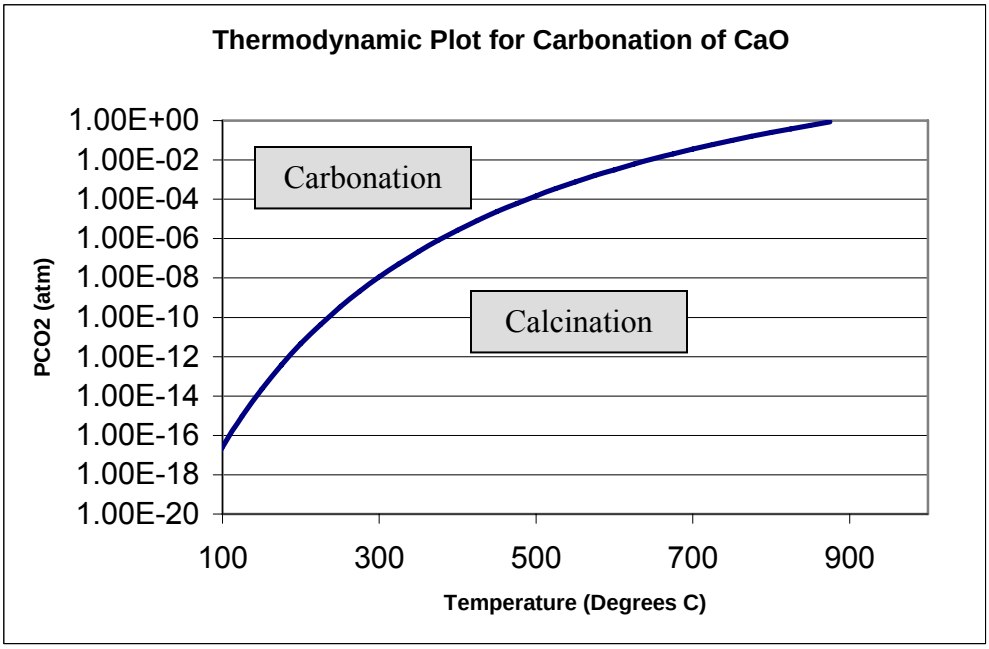

Figure 4.3: Thermodynamic Plot for Carbonation of CaO [1 atm total pressure]

Figure 4.3 shows that carbonation can still occur even above 875 ºC as long as pure streams of CO_2 are fed into the system. This allows for the system to be run at a temperature such that the CaO sorbent remains dehydrated, yet carbonation is highly favored.

Finally, in order to assess the feasibility of in-line regeneration of CaO with acetic acid, the thermodynamics of acetate formation were also studied. Since the reaction can potentially be enhanced by combined hydration and acetate formation, and since H_2O is a product of the reaction, the thermodynamics of the system was studied at numerous partial pressures of steam. The results of thermodynamic analysis are below:

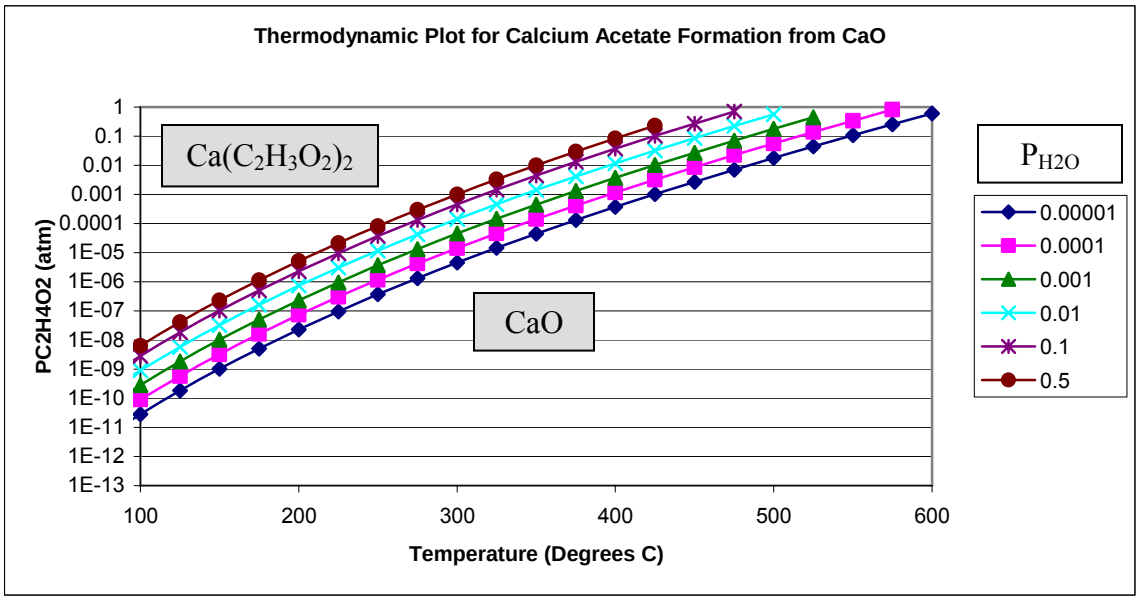

Figure 4.4: Thermodynamic Plot for $Ca(C_2H_3O_2)_2$ Formation [1 atm total pressure]

This plot shows that formation of calcium acetate is possible at elevated temperatures, up to and above 400 ºC. This realization has broad reaching impacts on the formation of calcium acetate in industrial regeneration scenarios for clean coal applications.

4.3 Effects of Pretreatment on CO_2 Capture Capacity

In order to assess the viability of eggshell as a sorbent for use in the calcium looping process, there are numerous critical considerations. Because eggshell is a natural bioceramic and is able to be used as an agglomerated sorbent, its removal from fly ash in the combustion stream will provide advantages over more finely powdered sorbents. Though this characteristic is important for industrial viability, perhaps even more important is the ability of the treated eggshell to effectively capture CO_2 once employed in the full-scale system.

As was discussed in the Technological Review, it has been postulated by Sasaoka et al. that the treatment of high temperature limestone sorbents with acetic acid vapors can increase reactivity from a "swelling" phenomenon of the pore structure. In order to understand the fundamental effect of acetic acid treatment on the surface of eggshell, the samples were imaged using a Quanta 200 scanning electron microscope. The images from fresh eggshell and eggshell pretreated with acetic acid can be seen below:

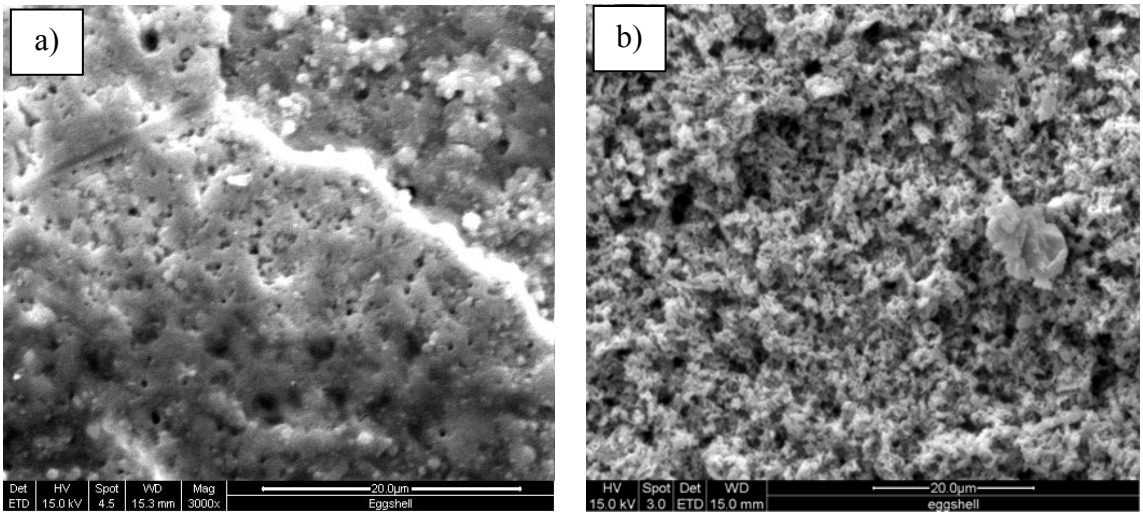

Figure 4.5: a) Image of Untreated Shell b) Image of Shell Treated for 30 Minutes with 2M Acetic Acid

This figure clearly depicts a stark difference between treated and untreated eggshell. The untreated eggshell in Figure 4.5 a) exhibits a very small surface pore structure. Though cracks are observed, diffusion into the sorbent would prove extremely difficult while utilizing this sorbent in commercial calcium looping applications. By contrast, Figure 4.5 b) exhibits a much more open pore structure for the calcium carbonate sorbent. This structure will help to enhance reactivity over numerous cycles as carbon dioxide diffuses through the more open pore structure to adhere to available surface sites.

Due to the solubility of calcium acetate in water, it seems as though the calcium acetate formed in the pretreatment of the shell is carried away from the shell's surface into solution. This was corroborated by measuring the mass of the shell before and after treatment. This theory is also supported by thermogravimetric analysis when looking at the calcination portion of plot, which will be shown more explicitly in Figure 4.7. The dissolution of calcium acetate helps to generate the pockmarks in the surface structure of the sorbent that assist in the multicyclic capture of CO_2.

The inside portion of the shell was also imaged. It can be seen below in Figure 4.6 that some of the membrane fibers remained attached to the inner surface of the eggshell. These fibrous structures were identified to be the membrane fibers of hen eggshells through testing on a scanning electron microscope [Yi et al., 2004]. This illustrates that, although most of the membrane is removed in the acetic acid treatment, small fibers may remain.

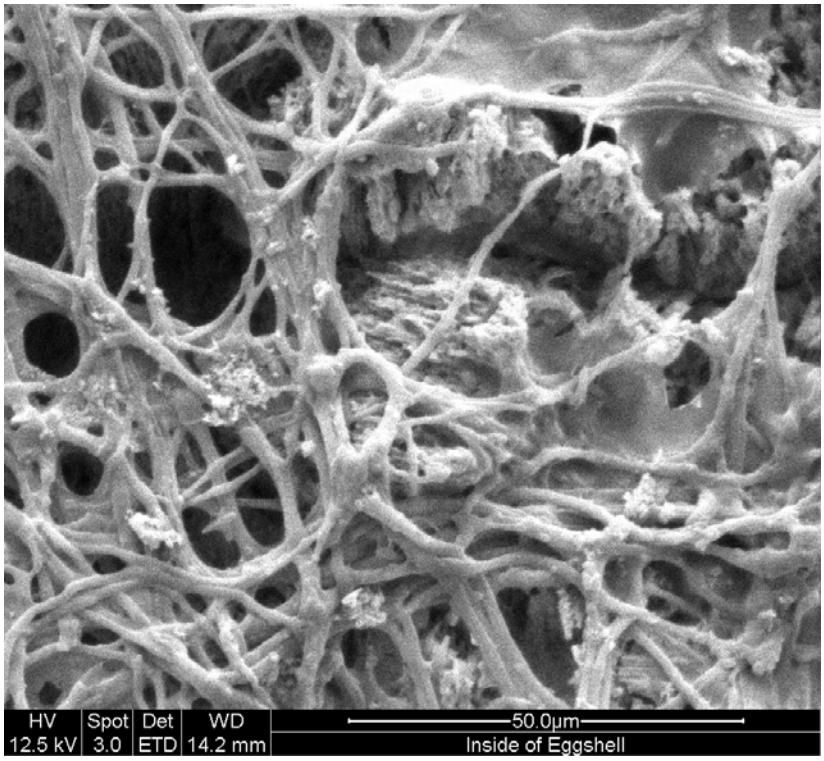

Figure 4.6: Inner side of Shell Treated for 30 Minutes with 2M Acetic Acid Displaying Membrane Fibers

As was discussed in the Experimental Procedure, the method employed to characterize the capture of the CO_2 involved subjecting the sorbent to cyclic carbonation calcination reactions after the treated eggshell was synthesized. This was completed by flowing a 10% CO_2 stream at 120 mL/min in a thermogravimetric analyzer. There is much that can be learned through employing this technique. These conditions, for instance, model typical operation in a gas-solid fluidized bed used for the water gas shift reaction in clean coal applications. The figure below illustrates the first cycle in the carbonation of eggshell with a 1M, 30 minute pretreatment with acetic acid:

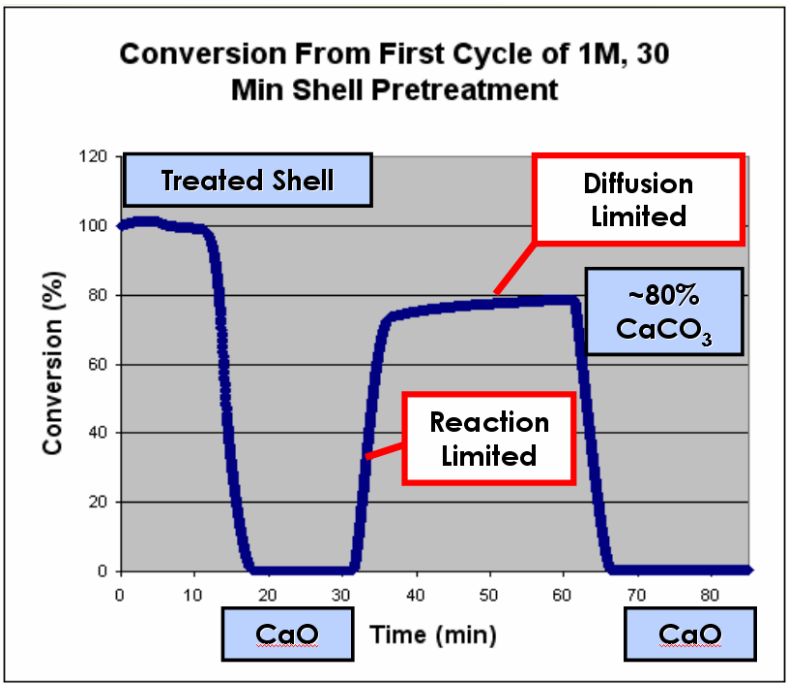

Figure 4.7: Conversion from the First Cycle of a 1M, 30 Min Acetic Acid Treated Eggshell

This figure displays several key features. In the first 13.5 minutes of testing, the temperature is steadily increased from 25 ºC to 700 ºC at 50 ºC/min. If the sample contained any calcium acetate, it would undergo several decompositions as the temperature was increased (this will be shown in Figure 4.11). This figure, therefore, shows that the sample at the start of the run is essentially pure $CaCO_3$. The shell then calcines at 700 ºC, forming pure CaO. Once the CO_2 flow begins, the reaction of CO_2 with CaO is reaction rate limited. At a certain point, as is predicted by mass transfer theory for diffusion controlled reactions [Middleman, 1998], all available surface sites for reaction are consumed. At this point the CO_2 must diffuse deep into the pores of the structure, causing a sharp decline in reactivity.

There are three key parameters to consider when assessing an optimal pretreatment for the eggshell sorbent. The first of these parameters is the conversion of the shell in the first cycle. The second involves the recyclability of the eggshell particles.

In order to minimize the parasitic energy wasted in heating and cooling the unreacted portions of the sorbents, as much of the sorbent as possible should react during each carbonation. This will help to increase the overall energy efficiency of the clean coal process. Finally, the cost in order to synthesize the sorbent should be minimized. This can be achieved through maximizing the recovery of collagen from the membrane and reducing the operating costs for purchasing acetic acid by lessening the volume of acid required. Previous studies of acetic acid pretreatment of eggshells focused on higher strength treatments; however, these studies all found that treatments with lower strengths of acetic acid (~2M) had the most favorable capture of CO_2 [Sparks, 2005; Vonder Haar, 2007]. In order to explore testing of these pretreatments more completely, experiments were carried out for 1M, 15 minute; 1M, 30 minute; 1M, 60 minute; 2M, 15 minute; and 2M, 30 minute exposure times. In order to capture the shell type with the best multicyclic activity and best first cycle activity, each of these combinations was tested in the TGA according to the experimental design discussed in section 3.2. The results of the averaged peak conversions for each of the first five cycles are shown below in Figure 4.8:

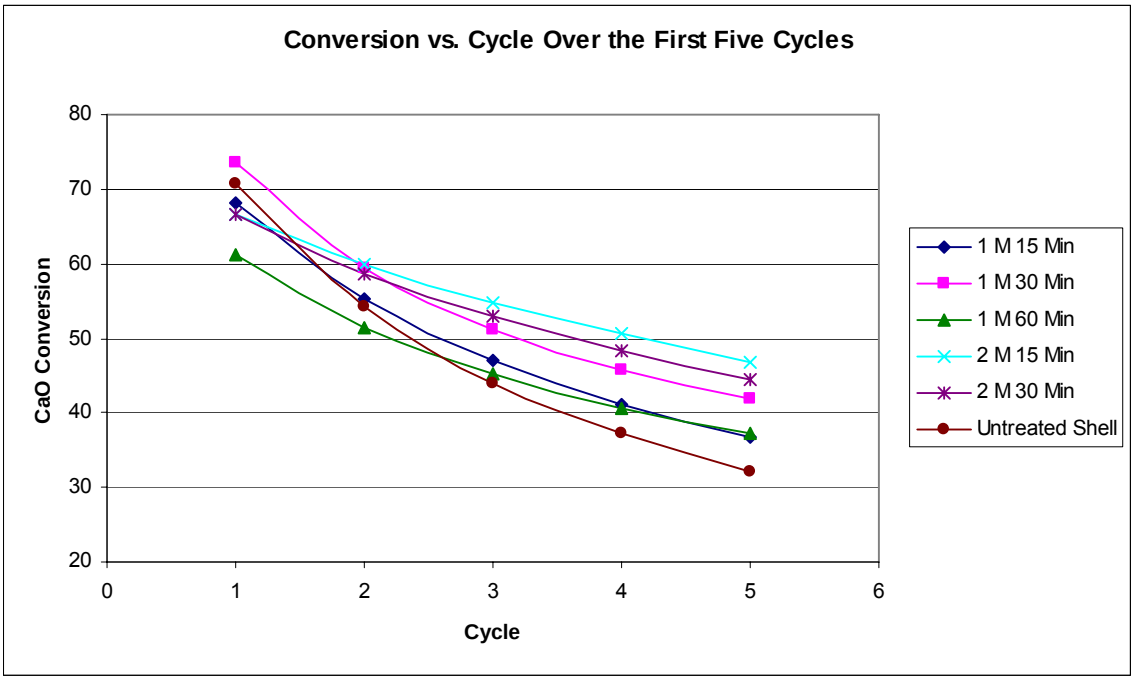

Figure 4.8: Conversion from the First Five Cycles for Varying Eggshell Pretreatments.

Based on the results in Figure 4.8, the best conversion in the first cycle occurs with eggshell treated with 1M acetic acid for 30 minutes. While this may be the case for the first cycle, subsequent cycles show that the 2M 15 minute acetic acid treatment provides the best long term viability after five cycles. This is followed closely by shell treated with 2M acetic acid for 30 minutes. After just five cycles, it should be noted that the optimal pretreated shell displays an almost 15% increase in conversion over raw shell, even though the raw shell performed better in the first cycle. This is due to the enhanced surface structure generated by acetic acid pretreatment.

4.4 Effects of Regeneration on CO_2 Capture Capacity

Due to the rapid decline in eggshell reactivity, regeneration of spent sorbents is the key to maintaining capture. Though this technique is specifically applied to eggshell sorbents, its application to any form of CaO sorbent is viable at elevated temperature, as

was proven in the thermodynamic analysis provided in Section 4.2. In order to characterize the effects of regeneration, numerous samples were prepared for thermogravimetric analysis. A range of regenerations were tested, including pure H_2O, 0.5 M, 2 M, 5 M, 50% , and glacial acetic acid. This technique was explored largely due to the large molecular volume of the calcium acetate molecule and literature that supported that calcium acetate offered an optimal starter molecule for CaO sorbent synthesis [Lu et al. 2006]. Because the calcium acetate molecule is large, when the particles calcine, they tend to form very large pores through which CO_2 can more easily diffuse over extended cycles.

In order to best illustrate the effect this change has on pore structure, several shells were imaged in a scanning electron microscope. Two sets of particles regenerated with 2M and glacial acetic acid respectively were imaged that had undergone three regenerations (after 5, 10, and 15 CCR cycles). These particles had undergone a total of 20 CCR cycles and were calcined. As a means of comparison, a shell was imaged that underwent only one calcination. To compare these to their respective regenerated versions, samples were also imaged that had undergone a total of 50 cycles and 5 regenerations (after 5, 10, 15, 20, and 50 cycles). These images can be found displayed below in Figures 4.9 and 4.10:

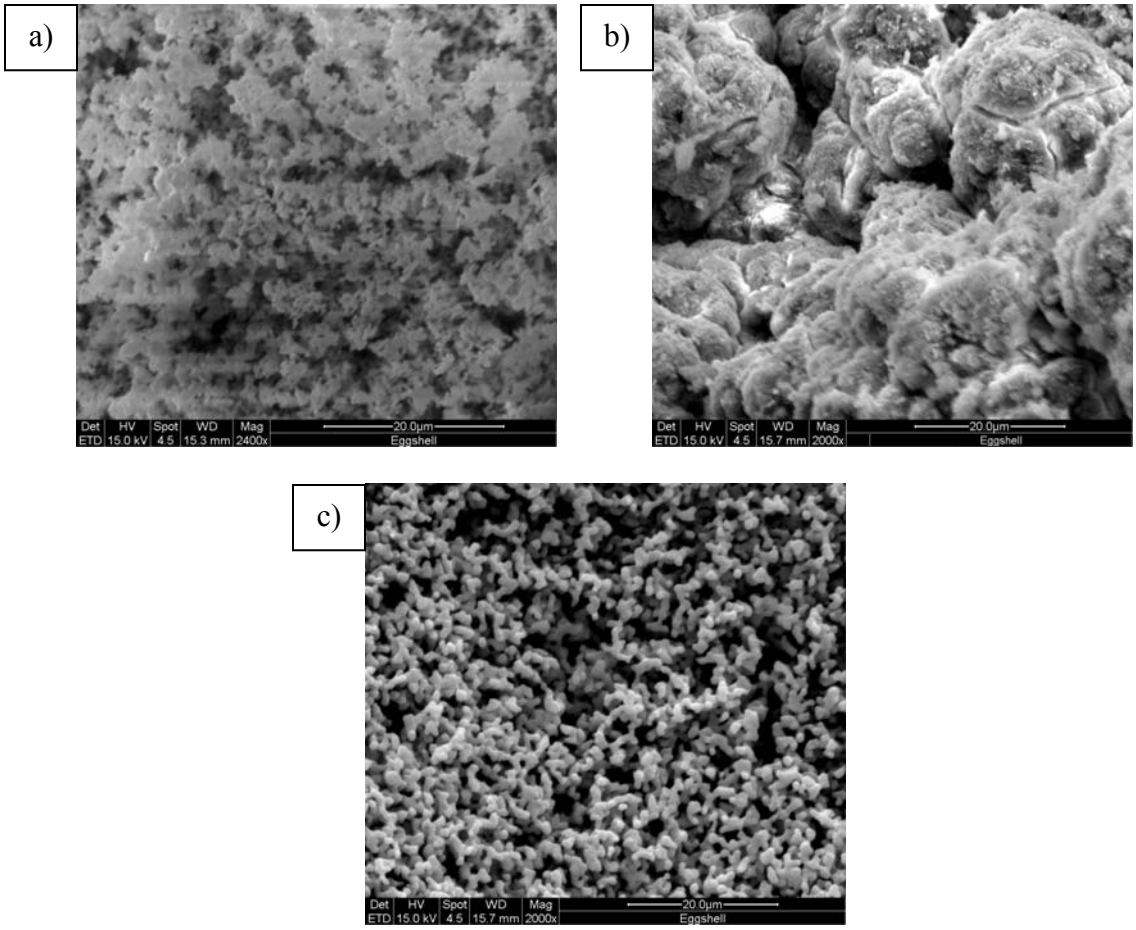

Figure 4.9: a) Eggshell after 1 Calcination, b) Calcined Eggshell after Three 2M Regenerations and 20 cycles c) Calcined Eggshell after Three Glacial Acetic Acid Regenerations and 20 cycles

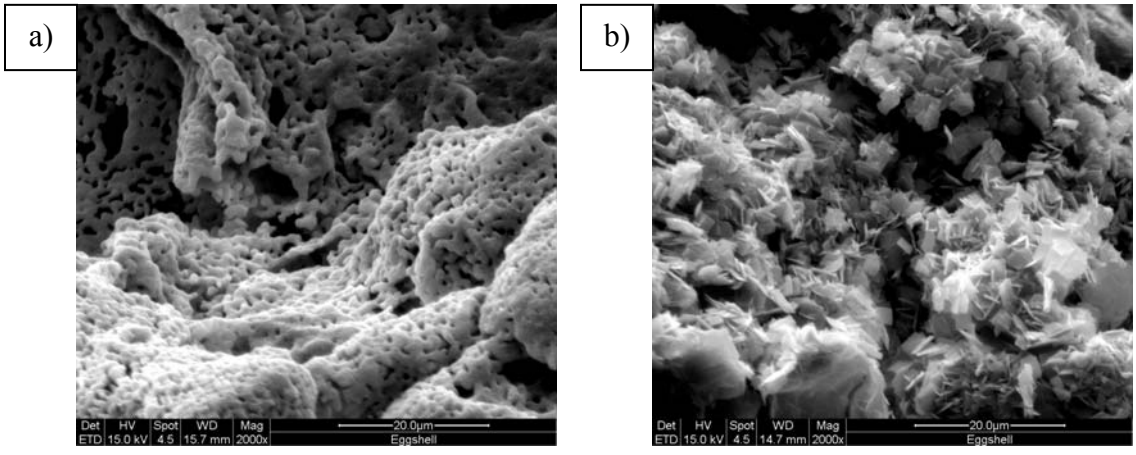

Figure 4.10: a) Regenerated Eggshell after Five 2M Regenerations and 50 cycles b) Regenerated Eggshell after Five Glacial Acetic Acid Regenerations and 50 cycles

These images offer very striking differences in surface morphology based on treatment and regeneration. The treated shell that is calcined shows a fairly open pore structure. The sample, after the third regeneration with 2M acetic acid, was observed to undergo an agglomeration to form a less porous sorbent after five additional CCR (Cycles 16-20) cycles. The sample that was treated with glacial acetic acid in Figure 4.9 c), however, displayed a very porous structure even five cycles after the previous regeneration (Cycles 16-20). Figure 4.10 a) shows the ability of the sorbent to restructure after regeneration with 2M acetic acid. The structure formed is much more porous and, due to the combined water and acetic acid, is able to restructure into a much different surface with numerous openings through with CO_2 can diffuse once the sample is calcined. The CaO regenerated with glacial acetic acid in Figure 4.10 b) displays the formation of calcium acetate crystals. Once the calcium acetate is calcined to CaO, the large decrease in molar volume opens up the pore structure of the sorbent for exceptional reactivity over numerous cycles.

The decomposition of calcium acetate to CaO is a well documented phenomenon. There are several phases over which the calcium acetate molecule decomposes. The molecule traditionally exists as a monohydrate at room temperature of the form $Ca(C_2H_3O_2)_2 \cdot H_2O$. It's decomposition from this form is addressed in the table below:

Table 4.1: Summary of Decomposition of $Ca(C_2H_3O_2)_2$ [Adapted from Panzer, 1964 and experimental data]

Temperature Ranges of Decomposition (ºC)	Phase Formed
80-150	Half Hydrate Formed
195-215	Amorphous and β-Anhydrous Forms
240-275	α-Anhydrous Forms
400-430	Decomposition of Ca(C2H3O2)2 to CaCO3
~675	Calcination of CaCO3

This can also be observed in the experimental data for tests which utilized the treatment of CaO with glacial acetic acid. This is exhibited in Figure 4.11 below:

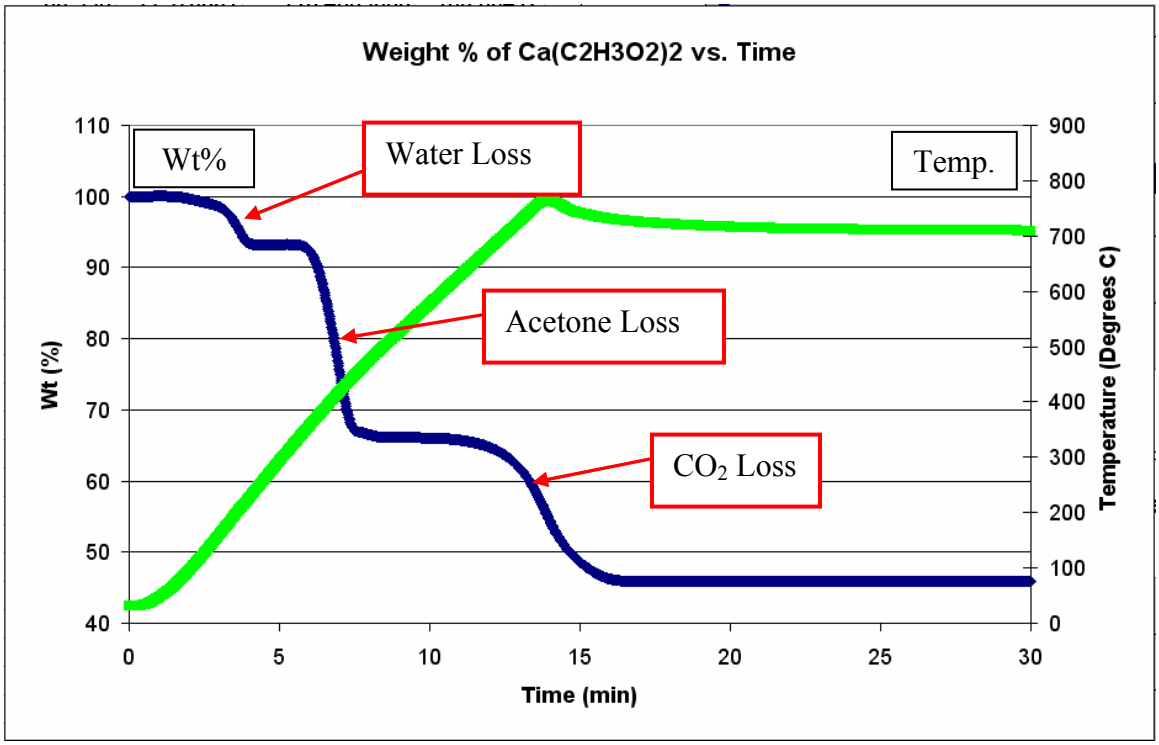

Figure 4.11: Thermal Decomposition of $Ca(C_2H_3O_2)_2 \cdot H_2O$ for Glacial Acetic Acid Treated Shell

This figure corroborates the findings for the atmospheric pressure thermal decomposition of $Ca(C_2H_3O_2)_2 \cdot H_2O$ found in literature [Panzer, 1964; Lu et al., 2006] and further reinforces the previous thermodynamic analysis that the regenerations for the spent CaO sorbent should occur at temperatures below 375-400 ºC. Because acetone is released in the decomposition of $Ca(C_2H_3O_2)_2 \cdot H_2O$, it is necessary to consider the fate of acetone in the industrial process. The spent CaO sorbent, once treated with acetic acid and steam, can be returned to the calciner for thermal decomposition, in which case acetone vapors must be separated out from the CO_2 product stream or sequestered with CO_2. Another possibility is for the thermal decomposition of $Ca(C_2H_3O_2)_2$ to $CaCO_3$ to take place in the lock hopper in which the calcium oxide would be regenerated by utilizing a temperature

swing after treatment to reach about 450 ºC. The calcium acetate would then be decomposed into calcium carbonate and could be returned to the calciner for calcination without the risk of acetone vapors entering the main circulation system.

In order to assess the optimal treatment for multicyclic sorbent regeneration, the sorbent was regenerated after five cycles until the sample had undergone a total of 20 total CCR cycles. This was done for all concentrations of regenerations for 1M, 15 minute and 1M, 30 minute pretreatments. Then, by assessing the optimal treatment based on economics and sorbent conversion, a best case treatment was discovered for regenerations. The resulting best case was then tested on the other three sorbent pretreatments utilized in this study. Depictions of each regeneration tested on the first two sorbent pretreatments are shown below in Figure 4.12 and 4.13:

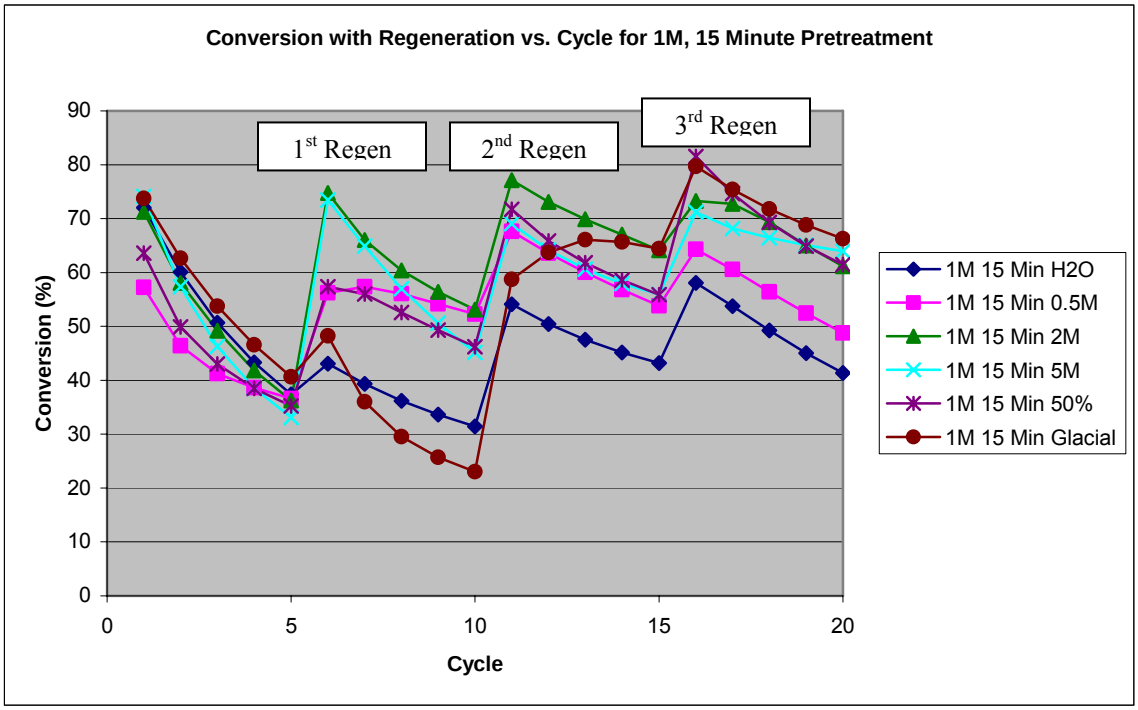

Figure 4.12: Conversion with Various Regenerations of Eggshell with a 1M, 15 Minute Pretreatment

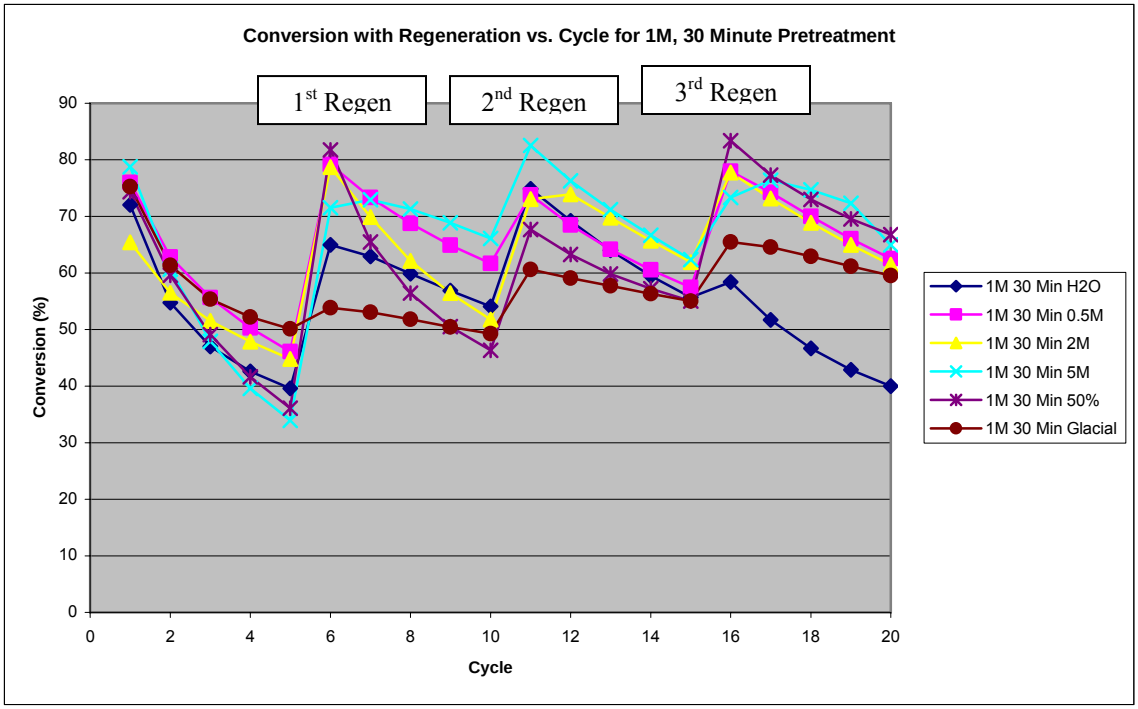

Figure 4.13: Conversion with Various Regenerations of Eggshell with a 1M, 30 Minute Pretreatment

These figures provide valuable insight into the role of regeneration on conversion. By looking at both sets of plots, general trends can be observed. First, it is noticed that regeneration with pure water provides the least effective regeneration of the sorbent when compared to techniques that also employ the use of acetic acid. This can be attributed to two facts: that calcium acetate has a higher molar volume than $Ca(OH)_2$ and that the combination of water and acetic acid allows for a surface structure rearrangement due to the solubility of calcium acetate in water. While this second effect can be attributed to sorbent restructuring at the low temperature range, when dealing with gas phase reactions, it is unclear to what degree surface molecules will be able to restructure. Also, from the graphs, it should be noted that pure acetic acid provides higher conversions with each additional regeneration, providing an incentive to use pure acetic acid in the treatment of spent sorbent. This being said, since acetic acid is more expensive than

water, especially at high purity, lower costs may be incurred by using lower strength acetic acid solutions. The best low strength method found for regeneration involves the use of 2M acetic acid as this offers sustained high conversions after each regeneration. In order to assess the role of pretreatment on capture over numerous cycles, the same regeneration was tested with each pretreatment. The graph showing the results for all 2M acetic acid regenerations is shown below:

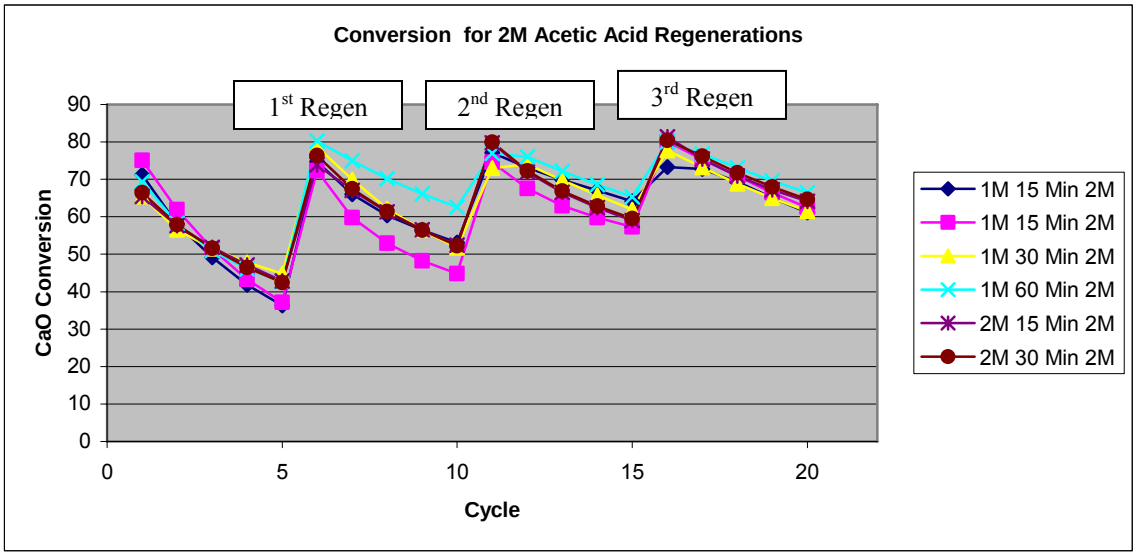

Figure 4.14: Conversion with Various Pretreatments and using 2M Acetic Acid Regenerations.

The results in Figure 4.14 show very encouraging results. First, it is clear that after three regenerations, all of the sorbent samples tested converge to similar results. This implies that acetic acid regenerations tend to erase the surface memory of the sorbent and cause the sorbent's capture to be more dependent on the regeneration than the initial pretreatment. Also, it is observed in this figure that both the first cycle and last cycle carbonation increase in conversion after each subsequent regeneration. This has very important implications for the viability of acetic acid regenerations in industrial

production because it shows that occasional regenerations can greatly increase reactivity of spent sorbent.

While five cycle testing offers a glimpse into the recyclability of the eggshell in calcium looping technologies, it is important to carry out longer cyclic studies in addition to these smaller cyclic treatments. For this reason, 30 cycle tests were carried out on three sorbents that showed promise for acetic acid regenerations and had already undergone 20 cycles. The eggshell was regenerated for the fourth time and allowed to undergo 30 additional CCR cycles. The results are shown below:

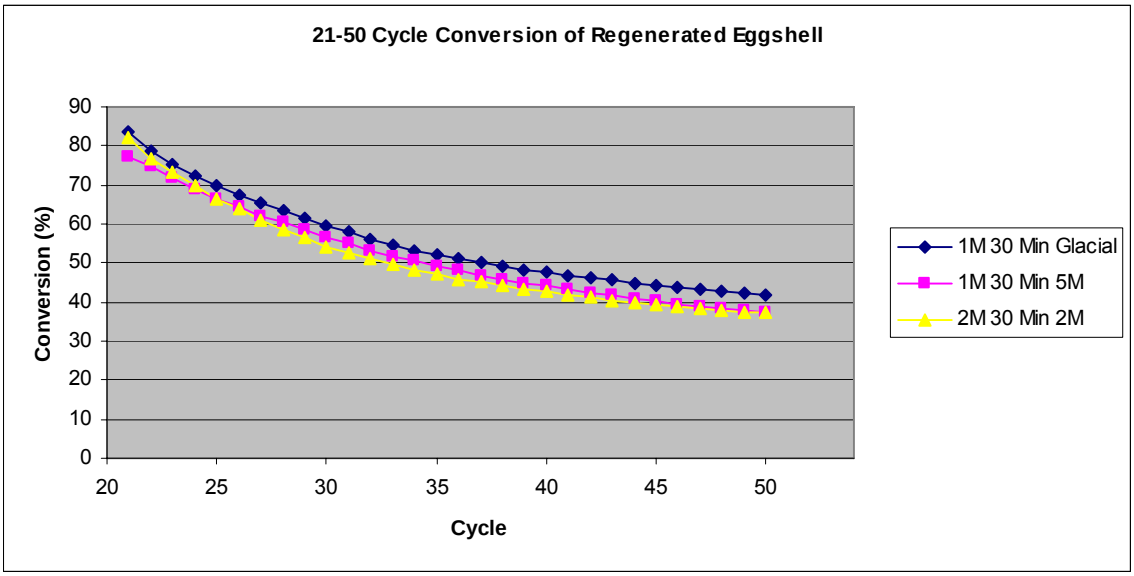

Figure 4.15: Conversions over the 21st-50th Cycles for Regenerated Sorbents

These results show that pure acetic acid treated eggshell continued to improve, offering the best conversion from the 21st through the 50th cycles. All of the sorbents, however, performed exceptionally well. Previous testing of eggshell with only pretreatment showed that conversion decreased to close to 18% for both 2M pretreated shell and 6M pretreated shell after just 15 cycles [Sparks, 2005]. The regenerated shell samples remain close to 40% conversion, even after 30 cycles, as is shown in Figure

4.15. This also compares favorably to Linwood Carbonate Fines (which decreases to 36% conversion over 25 cycles) [Iyer, 2004]. While synthetic sorbents, such as Precipitated Calcium Carbonate can achieve conversions of 53% over 30 cycles [Iyer, 2004], treated eggshell offers a lower-cost alternative.

When comparing these conversions with those achieved with untreated eggshell, the contrast is extremely clear, showing that the acetic acid regenerations offer a vast improvement on conversion. If the sample from Figure 4.15 that had undergone a 2M, 30 minute pretreatment with 2M regenerations was considered to be in its first cycle for the sake of comparison, an illustration of the contrast between its reactivity and that of raw shell can be seen below:

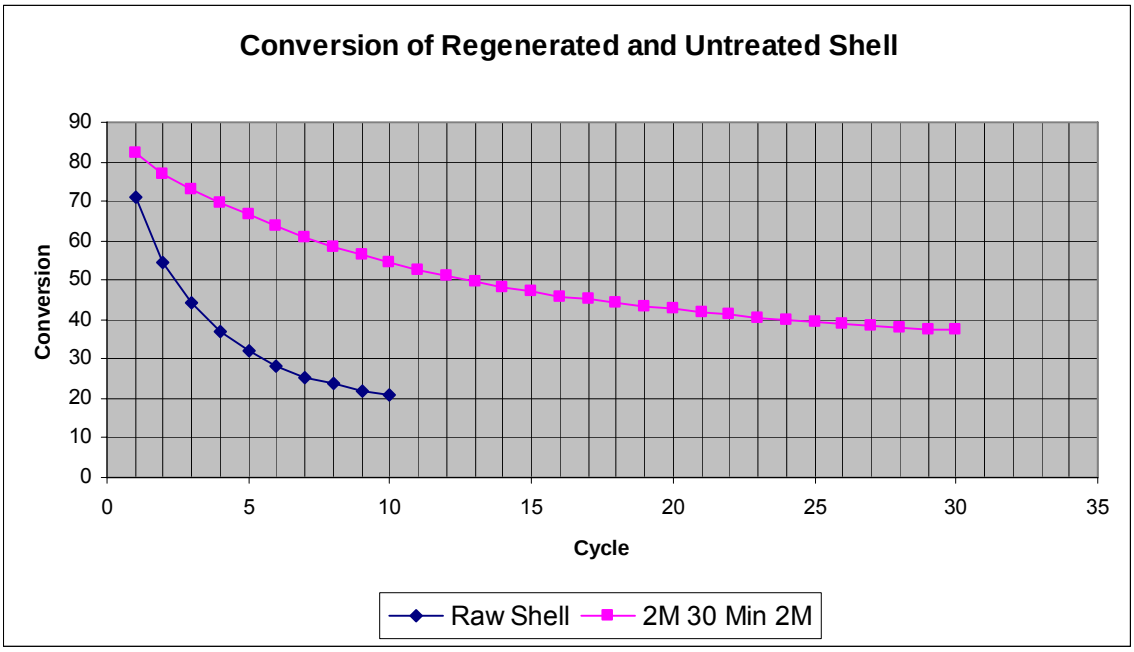

Figure 4.16: Conversions of Regenerated Sorbent Compared to Raw Shell

While the raw shell drops to approximately 38% conversion in just four cycles, the regenerated sorbent takes over 30 cycles to drop that low. This shows nearly an eightfold increase in recyclability for the particles after four regenerations.

4.5 Applications of Eggshell in Methane Steam Reforming

In addition to the role that effective calcium sorbents play in enhancing hydrogen production in syngas-based systems, they can also be used in combination with other fuel sources. As was suggested in the technological review, the use of CaO derived from eggshells can also be used in a variety of other scenarios. One such example is in the production of hydrogen from methane. In this case, the eggshell-derived CaO serves two purposes. The first purpose is to absorb the pollutant CO_2 from the reacted methane for separation of CO_2 and purification of hydrogen. The second reason is to pull the reactions to completion through employing Le Chatelier's Principle. Since equilibrium does not favor full conversion of methane to CO_2 in methane steam reforming, even with a steam to carbon ratio of five to one in the feed stream, the in situ removal of CO_2 allows for the reaction to be more fully completed. This not only increases H_2 yield, but it also helps boost hydrogen purity. To demonstrate this, 3g of crushed eggshell and 3g of Performax catalyst were used to reform methane. It is seen in Figure 4.17 that the system reaches over 99% H_2 purity and also leaves virtually no unreacted methane in the product stream while the sorbent is active. As can be seen, the amounts of CO_2 and CO are also at nearly undetectable levels while the eggshell sorbent is active. In an industrial system, a fluidized bed could be used for the purposes of enhancing mass transfer and allowing for efficient change out of spent sorbent concurrently.

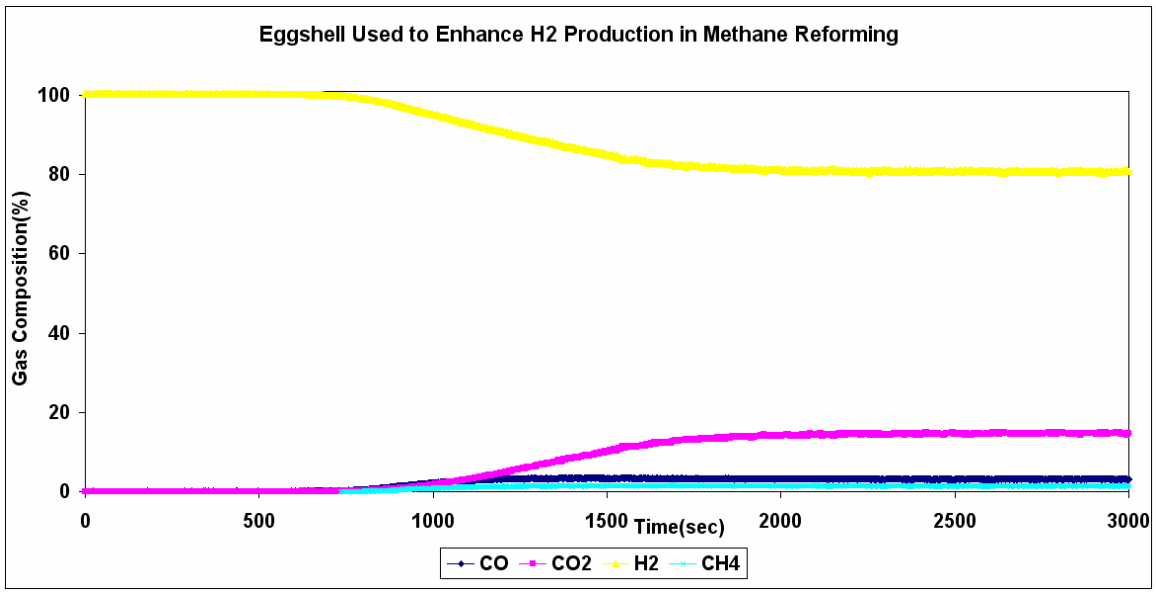

Figure 4.17: Eggshell Used to Enhance Hydrogen Production [650 ºC, 5:1 Steam:Carbon Ratio, 0 psig]

4.6 Removal of Collagen from Eggshell Membranes

As mentioned in the Technological Review, eggshell membranes are a good source of collagen in addition to numerous other proteins. Effective separation and purification of collagen derived from eggshell membranes offers a significant economic incentive to pursue the purification of collagen and pretreatment of eggshell with the appropriate acetic acid mixtures. In order to assess the availability of collagen in the eggshell membrane, samples were sent to The Ohio State University Mass Spectrometry and Proteomics Laboratory. At first, since proteins, including collagen, are typically dissolved in acetic acid for further testing and for differential salt precipitation [Rucklidge et al., 1996], it was thought that a substantial yield of collagen could be lost during the membrane pretreatment phase. For this reason, the acetic acid used in pretreatment was tested for the presence of collagen. Even after concentrating the samples, no collagen was found in the samples taken. This indicates that the amount of

collagen lost in this stage may be minimal compared to the amount of collagen in the membrane. When testing the membranes themselves, type X collagen was identified after it was isolated via gel electrophoresis. The tested sample had a band for type X collagen; however, it was present in somewhat small quantities. Quantitative separations and purifications are currently in progress for the testing of column chromatography using a heparin column in addition to differential salt precipitation to separate out type X collagen and other collagen types more economically and more completely.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The results of the conducted experimentation offer numerous useful pieces of information towards the integration of waste eggshell processing into clean fossil fuel conversion techniques. First, by analyzing the structure of the shell before and after acetic acid pretreatments, it can be seen that acetic acid has dramatic effects on the surface morphology of the shell. By enhancing this structure, the long term reactivity of the shell can also be enhanced.

It was determined from testing that 2M, 15 minute pretreatments offer the best treatment for enhancing the surface structure of the shell for multicyclic operation in a commercial clean coal facility while 1M, 30 minute treatments offer the best first cycle conversion on average. Contrary to prior findings, these mixing times were sufficient for lab scale membrane removal due to the fact the shells were not allowed to dry out before being processed. This can be easily instituted in an industrial facility by having a water-filled holding tank.

Next, applying 2M acetic acid regenerations to the shells allowed for a dramatic improvement in the pore structure of the particles. This led to drastic regenerations of sorbent activity and enhanced recyclability of regenerated particles. By looking at the thermodynamic analysis, it can also be seen that the process can be completed at temperatures of approximately 400º C. This allows for an efficient means of sorbent regeneration to be incorporated into industrial systems for not only eggshell but also other CaO sorbents that fall victim to pore collapses.

By being able to generate this enhanced sorbent structure, the CaO from eggshells can be utilized in numerous commercial settings. In addition to simply acting as a sorbent to pull reactions to completion in the traditional chemical looping processes, CaO can also be used as a sorbent to increase yield and purity of hydrogen from the methane steam reforming process. The CaO sorbents investigated can also be used to capture CO_2 from flue gas generated from traditional pulverized coal combustion; however, clean coal techniques employing gasification tend to increase the efficiency of the whole CO_2 capture process due to their ability to operate at elevated temperatures and pressures as well as employing the chemical intermediates in the looping process set-up.

Finally, it was established that type X collagen is present in the membrane of chicken eggshells, in addition to numerous other proteins. These proteins can either be separated and purified in more expensive industrial techniques, including column chromatography, or the membrane can be fully dissolved and sold as a cell-culture scaffold. All of these options greatly enhance the process economics of the membrane removal process and shell pretreatment.

5.2 Recommendations

While much was able to be established through the initial testing on eggshell pretreatment and acetic acid as a means of regeneration, there is still much more to learn. Of highest importance for the industrial feasibility of the process is the testing of high temperature acetic acid regenerations to verify that the same regeneration phenomena is encountered at high temperature.

Also, even though the use of acetic acid in regenerations of eggshell has been proven as feasible, the phenomenon should be explored for its effects on the recyclability of other calcium sorbents, including limestone. Limestone is a cheap source of lower reactivity calcium; thus, by utilizing this regeneration scheme, there may be room to improve the mechanics of this process for all calcium sorbents. It would also be very useful to quantify the effects of different treatments on pore structure while utilizing a BET Analyzer. This would help to further characterize surface area and pore volume of reactive calcium sorbents.

Also critical is further exploration of the various methods of collagen extraction and purification that are available for the industrial scale. Although column chromatography and differential salt precipitation arose as good initial options, testing their feasibility and the collagen purity produced are key concerns. While testing is still ongoing to test these techniques at the Ohio State University Mass Spectrometry and Proteomics Lab, additional follow-up is required to help quantify collagen yield at different conditions.

In summary, this is a very promising technique that, with further study, has the potential to revolutionize eggshell waste treatment in commercial egg processing facilities and holds great promise for the advancement of all calcium based clean fossil fuel conversion technologies.

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